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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS,
ERNEST MERRITT, and FREDERICK BEDELL

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MAY, 1911

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THE

PHYSICAL REVIEW.

ON THE FREE VIBRATIONS OF A LECHER SYSTEM, USING A BLONDLOT OSCILLATOR.[1]

By F. C. Blake and Emma A. Ruppersberg.

Introduction.

THE distribution of energy along Lecher wires in air was first quantitatively studied by Rubens.[1a] By means of the bolometer he showed that the wave system set up in two parallel wires under certain conditions consists of the free vibrations of those wires. Later Apt[2] studied the influence of the exciter upon the form and intensity of the electrical vibrations of the Lecher system. Among other things he showed that the lead wires from the induction coil to the oscillator played an important part. He obtained the strongest effects when complete resonance existed among the four circuits of the system concerned: viz., secondary binding posts of induction coil to oscillator, oscillator to primary Lecher plates, secondary Lecher plates to bridge of Lecher system, bridge to end Leyden jars. Apt states, moreover, that the intensity of the waves of a given length set up in the parallel wires depends upon the form of the oscillator and the conditions controlling the production of the primary spark. He discusses the relative merits of the two forms of oscillators, the Lecher and Blondlot types, and comes to certain conclusions to which Drude[3] has taken exception. In stating his objections Drude discusses the mode of action of the Lecher

[1] Read at the Chicago meeting of the American Physical Society, Nov. 26, 1910.

[1a] Rubens, Wied. Ann., 42, p. 154, 1891.

[2] Apt, Wied. Ann., 61, p. 293, 1897.

[3] Drude, Wied. Ann., 61, p. 631, 1897.

system and shows that the character of the wave system is far more important than the production of a large potential difference in the first loop behind (*i. e.*, toward the bolometer end of the Lecher system) the fixed bridge. In other words, he says that system of waves is best and most characteristic which makes the ratio of intensities for a loop and for a node the greatest possible. Drude was, of course, aware that not all induction coils work equally well in the production of wire-waves, a thing many experimenters have found. He showed, however, that if one connects the wires which lead from the induction coil to the vibrator as close as possible to the spark-gap he then becomes in some measure free from the effects of the induction coil upon the wave-system in the parallel wires.

Coolidge[1] modified the original Blondlot oscillator by inserting a sheet of mica between the primary and secondary turns, thereby enabling him to obtain very much stronger oscillations by reason of the greater induction. He was disturbed, however, he says, by the presence of strong mechanical vibrations in the secondary if an influence machine was used as a source of power. He tried to get rid of this disturbance by introducing a second spark-gap in oil, but did not succeed.

The experiments described in this paper were undertaken in an endeavor to study the wave system in the Lecher wires using a Blondlot oscillator as exciter and a Rubens bolometer as detector. To be as free as possible from the influence of the induction coil upon the oscillator it was thought wise to introduce two side sparks in air after the manner of the Righi vibrator. This has of course the advantage of symmetry over the Drude-Coolidge single side-spark in oil.

One cannot study the literature on this subject of wire waves without wondering whether the different experimenters[2] were always sure in their own minds of the character of the oscillations with which they were working. We find it difficult, for instance, to tell in certain cases from the published accounts whether the oscillator was forcing its own system of vibrations upon the parallel wires or whether they were swinging freely. It seems best to defer

[1] Coolidge, Wied. Ann., 67, p. 578, 1899; 69, p. 125, 1899. See also Hormell, Phil. Mag., 3, p. 52, 1902, or Am. Journ. Sci., 12, p. 433, 1901.

[2] Coolidge, *l. c.*

a critical discussion of this and other points however until after our own experimental results are presented. As the experimental development may be of interest the results are presented in the order in which they were obtained.

Description of Apparatus.

The Blondlot oscillator (Fig. 1) was a modification of the form used by Coolidge and by Hormell.[1] The primary consisted of two semi-circular brass wires PP' (diameter 2.08 mm.) enclosing a circle of 4.8 cm. diameter, with an opening of 2 mm. at k and a spark-gap at a. The balls bb' were of brass of 6.36 mm. diameter with a

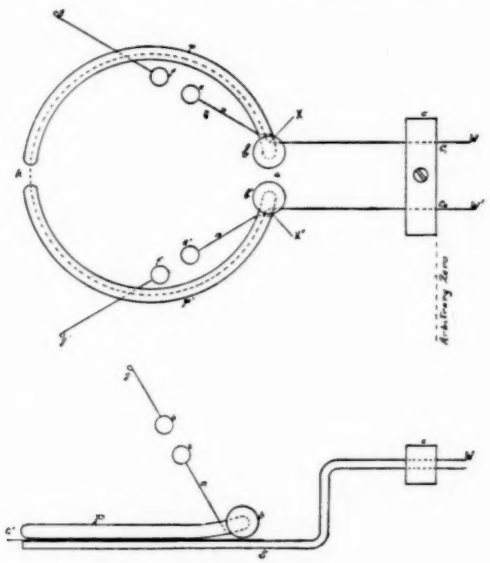

Fig. 1.

hole bored in each radially and made to fit the ground ends of the primary wires PP' very tightly. In this way each ball could be turned on its diameter as an axis, thus leaving a new surface to be exposed whenever necessary and yet remaining immovable when the spark was passing, as well as retaining a constant position relative to the secondary circuit after being turned. Before any one curve was taken a new portion of the balls was turned toward

[1] Hormell, *l. c.*

the spark-gap. For such a spherical ball spark-gap the length of the gap rapidly increases at first as the discharge passes and tears off the brass and hence at first the oscillator deterioration is more rapid than after the oscillator has been in use a short while. Accordingly, to avoid this rapid initial deterioration when a new portion of the brass was exposed the circuit was always closed at least twenty times before readings were commenced. After that the oscillator deterioration was quite slow and uniform and could readily be taken into account. This was done for all the curves except where specified by choosing some position on the Lecher wires as a check point at which every sixth reading was taken.

The air-gap balls *ee'* and *ff'* were smaller in size, being 4.2 mm. in diameter, *ee'* being attached to brass wires *mm'* 14 mm. long and 1.3 mm. diameter. Following Drude's suggestion of partly freeing the vibrator from the influence of the induction coil, the wires *mm'* were riveted into *PP'* just as near the balls *bb'* as possible. The balls *ff'* were soldered to wires similar to *mm'* whose other ends *gg'* were looped for attaching the copper lead wires from the secondary of the induction coil.

The secondary circuit *SS'* of the oscillator consisted of brass wire of 1.4 mm. diameter and total length c_1kc_2 of 29 cm. up to the point where the meter stick readings began, that is, the point where the Lecher wires proper *WW'* were soldered, the whole being supported at the junction by a clamp of soft wood. This secondary circuit had the same diameter as the primary, forming a closed circle with the exception of 1.5 cm. just below the spark-gap of the primary. It was firmly cemented to the bottom of a shallow glass vessel by means of water-glass and was separated from the primary circuit by a sheet of mica 0.016 mm. thick. By means of a wooden support pressure could be applied from above and thus hold the two circuits rigidly touching the mica, the wires *PP'* being bent slightly upward near the balls to permit this. A small support equal in thickness to the secondary wire of the oscillator had to be provided for the mica sheet at the center to prevent its bending under the applied pressure. The glass vessel was supplied with a running stream of kerosene oil. To prevent oil splashing up on the air-gaps when the discharge passed they were protected by glass tubes.

The Lecher system consisted of copper wires 0.67 mm. in diameter which were kept scrupulously bright and polished and at a fixed distance of 2 cm. apart. Their free ends were passed through a support of soft wood 2 cm. thick against which the small Leyden jars pressed. These jars were made of glass tubes 2.9 cm. long of inner bore slightly greater than the diameter of the Lecher wires; their outer diameter was 7 mm. The wires leading from the jars to the bolometer were wrapped as a single turn around the jars at their center. The parallel wires were kept under a constant but unknown tension during the early part of the work. Later a known tension of 2,500 grams was used. A preliminary experiment showed that this tension could not be reduced much below 2 kilograms and have the readings constant for a fixed position of the bridge. Of course, in applying it all metal had to be avoided in the neighborhood of the Lecher wires, so it was done by means of a strong fishline working over pulleys. The bridges were all of the same diameter as the Lecher wires. They were 3 cm. long and bent downward at the ends at right angles to their length. To insure good contact they were weighted at the middle by a cord and plumb-bob.

As a source of power a 110-volt, 60-cycle alternating lighting circuit was used supplying by means of a control rheostat about 8 amperes to the primary of the 8-inch induction coil used. Except when expressly stated otherwise the coil was run directly on this circuit without condenser or interrupter. Two coils of about equal size (4-inch) were available and when for any reason one did not suffice the two were used. In this paper the two together will often be spoken of as a single coil except where possible confusion might result.

The bolometer used was very similar to the Paalzow-Rubens'[1] instrument, the quadrilaterals being constructed of iron wire of diameter 0.0208 mm. Following Rubens and Ritter[2] its sensitiveness was measured as 0.0001934° C. The usual precautions were taken against temperature variation by enclosing it entirely in a soft wooden box filled with cotton packing.

[1] Wied. Ann., 37, p. 529, 1890.
[2] Wied. Ann., 40, p. 55, 1890.

The galvanometer was a Leeds and Northrup four-coil Thomson instrument with a resistance of 7.78 ohms in parallel, and a sensitiveness of 1.55×10^{-8} amperes for a complete swing of 4.4 seconds.

It was found by trial that when the oscillator was set into action and the galvanometer was not shunted a rather large deflection (in some cases as high as 50 scale divisions) could be obtained when the wires leading to the bolometer from the Lecher system were removed. Further testing showed that the effect was not due to any direct action of the induction coil on the galvanometer but instead to diffuse radiation influencing the bolometer. As the walls of the room in which the work was carried out were constructed of metal lathing unusual care had to be exercised to be free from extraneous disturbances. By enclosing the bolometer with its accessories in a metal box the effect was considerably diminished. There was still some effect present when the bolometer was fully enclosed and it was located finally as due to stray radiation running back along the wires between bolometer and galvanometer, thus upsetting the bolometer balance and producing a throw. This was got rid of by wrapping these wires with tinfoil and earthing it together with the galvanometer case. Of course, for actual work there had to be an opening in the bolometer box for the wires from the Leyden jars of the Lecher system. As soon as these wires projected even a few inches above the box a large galvanometer throw was obtained when the oscillator was running. It was at once evident that the wires leading from the Lecher system to the bolometer had to be protected from the stray radiation. Trial showed that 10-inch furnace pipe allowed about 95 per cent. of the energy to travel along the wires if they were held in place along the center of the pipe by wooden supports, so this was done. By means of elbow joints in the pipe all the wire except about a foot immediately above the Leyden jars was thus protected. Not to be disturbed by capacity effects we deemed it unwise to run the protection piping any closer. We express it as our belief that a part of the deflection shown at the minima of the best curves shown below is due to stray radiation. We are not able to say, however, how much of the deflection at such minima is legitimate, that is, due to the energy following the Lecher system on to the bolometer wires, and how

much is extraneous. Accordingly we were unable wholly to correct for this error though we feel sure it was in all cases well within 5 mm.

Results.

In one of the early experiments using an oscillator somewhat larger than that described above and employing a Wehnelt interrupter attached to a single induction coil an attempt was made to obtain a system of nodes and loops on the Lecher wires in the case where the wires leading from the coil were metallically connected to the oscillator close to the spark-gap. How successful the attempt was is shown in curve *I*, Fig. 2. Here the Lecher wires were about 175 cm. long measured from the arbitrary point near the oscillator. The wire system was searched by means of a single bridge with the detecting Leyden jars at the ends. Plainly there is present nothing marked, although the galvanometer deflection without a bridge on was 200 divisions. Measurements were not continued beyond 104 cm. for it was evident that nothing characteristic would develop. Then a side-spark in air was introduced on either side of the oscillator as described above, and, still using the Wehnelt interrupter, Curve *II* of the same figure was obtained. Each point shown is the mean of from two to three readings that agreed fairly well (*e. g.*, 176, 166, 170) with each other.

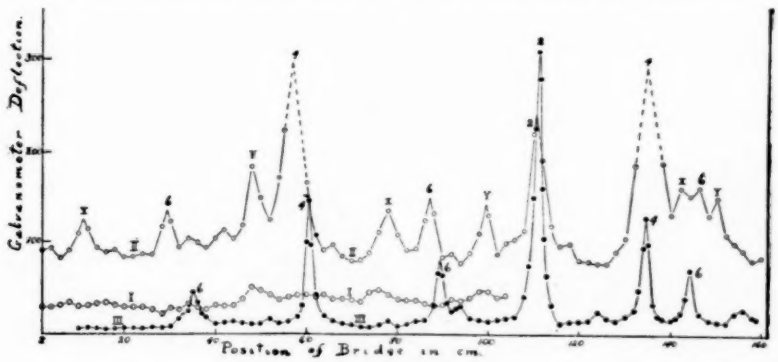

Fig. 2.

The two highest peaks are drawn partly dotted as the actual readings were off the scale. There can be no question as to their location, however, for enough of the slope for each was obtained to make their position approximatey correct.

Now it is well known in such work as this that the employment of a second and third bridge will enable one to determine what nodes respond to each other, and so other bridges were tried. This process revealed response between those nodes marked with the same number or letter. It was tried in the following way. The first maximum of a given type nearest the oscillator was carefully redetermined using smaller steps than 2 cm. and taking more readings for a given position; the true location of the maximum was thereby determined. Then a second bridge was similarly used to explore the wires further along and its correct position having been found a third bridge was used. Without exception in every case in which this was done it was noted that by employing a second bridge the second maximum of a given type was displaced slightly toward the oscillator compared with its position when a single bridge was used. This was true also of the third maximum. In other words, the internodal space is slightly shortened by the use of a second bridge. Unfortunately the maxima *Y* of Curve *II* were not tried for responses but there can be little doubt, we think, that they would respond to one another and so we have marked them as belonging to the same system. Further discussion of Curve *II* is temporarily reserved.

As the Wehnelt interrupter requires considerable attention from time to time it was thought worth while, following Blake and Fountain,[1] to use the alternating current direct upon the induction coil, without condenser and interrupter. When this was done, however, instead of giving a good system of nodes and loops such as Curve *II* shows, the nodes practically disappeared and we had Curve *I* over again.[2] Before resorting again to the Wehnelt interrupter, however, it seemed worth while to try a few variations.

Accordingly, following Berg,[3] three changes were made, the second of which proved of far greater importance than either of the other two, though each seemed helpful. First, a condenser was used between the induction coil and the exciter as shown in

[1] Blake and Fountain, PHYS. REV., XXIII., p. 257, 1906.

[2] The air-gaps were kept the same as for Curve *II*, 5 mm. say. At this stage the importance of knowing them accurately was not appreciated. They were probably between 4 and 6 mm. in length.

[3] Berg, Ann. d. Phys., 15, pp. 317, 318, 1904.

Fig. 3. Only a single condenser was used as shown, whereas Berg used two, one in each lead wire of the secondary coil. The condenser consisted of an ordinary piece of sheet glass with an area

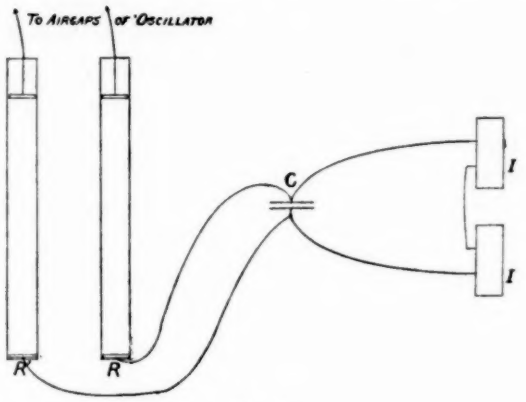

Fig. 3.

of lead foil 28 by 8 cm. in size on each side. Secondly, a variable water resistance was introduced between the condenser and the oscillator as shown in the same figure. In the third place, a metal screen with a circular aperture 18 cm. in diameter was introduced around the Lecher wire system but near the oscillator. The plane of the screen was at right angles to the parallel wires and symmetrically placed with respect to them. Although put in quite a different place from the two screens used by Berg it served the same purpose as his, viz., to lessen the direct action of the oscillator upon the detecting system.

With these changes made the node system was sought for on the parallel wires of length 154 cm. Good nodes were located at 31.2 and 83.5 cm.; the latter by use of a second bridge giving apparently 52.3 for the internodal space. Thinking these nodes[1] due to the oscillator and trying to allow for the end capacity due to the Leyden jars it was figured that the parallel wires should have a length of 160.4 cm. to respond best to the oscillator. Accordingly they were lengthened to 165 cm. since if too long they could be readily shortened. Further experimentation showed at

[1] The evidence was not yet at hand for knowing the relationship between the various "systems of nodes" of Curve *II*, Fig. 2.

once that the nodes shifted with every change in the length of the parallel wires. This meant of course that some of the nodes at least were those due to the free vibrations of the Lecher system and so a thorough search was begun.

Leaving the system 165 cm. long a series of curves was taken whose object was to find the influence of the air-gap length upon the Lecher vibrations. For measuring the gap-lengths a Brown and Sharpe thickness gauge was used. The method was of course not very correct but for the air-gaps at least it answered well enough as small changes in their length apparently did not appreciably affect the vibration system.

A typical curve obtained in this way is shown in Curve *III*, Fig. 2. Here the air-gaps were each 1.4 mm. long, while the oil-gap was 0.1 mm. long. The water resistance was each a column of rain water 30 cm. long and 2.5 cm. in diameter.

Remembering that a Lecher system using a Blondlot oscillator is closed at the vibrator end, we should expect[1] it to vibrate freely as shown in Fig. 4. Interpreted in the light of our detecting system Fig. 4 becomes Fig. 4*a*.[2] Plainly Curve *III*, Fig. 2, is an

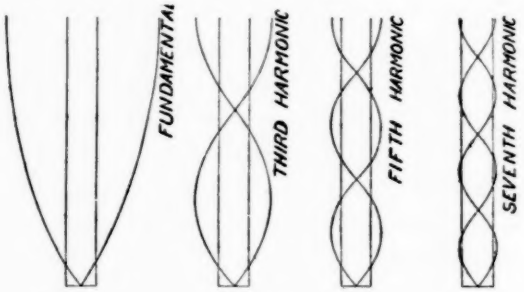

Fig. 4.

approximation to this ideal case. The fundamental tone is, of course, that represented by the galvanometer deflection when no

[1] See M. Abraham, Theorie der Elektrizitat, Vol. 1, p. 352, second edition.

[2] In Fig. 4, following the current practice in alternating current work the harmonics are denoted as *odd* harmonics. In Figs. 2 and 4*a* these same harmonics are marked as *even* harmonics. For instance the seventh harmonic of Fig. 4 is marked 6, 6, 6 in Fig. 4*a*. Unquestionably the latter notation is the only logical one, but for the sake of certain readers it seemed advisable to use here the double notation. Personally we prefer to have the word "harmonic" *exclude* the fundamental tone.

bridge is used on the Lecher system. Using a bridge the highest maximum at 111.3 was 40 per cent. of the reading for no bridge. Further theoretical discussion is reserved till later. The principal maxima of Curve *III* correspond then to the free vibrations of the Lecher system; the first overtone at 111.3, the second overtones at 60.7 and 134.7, the third overtones at 35.3, 89.7 and 144.3.

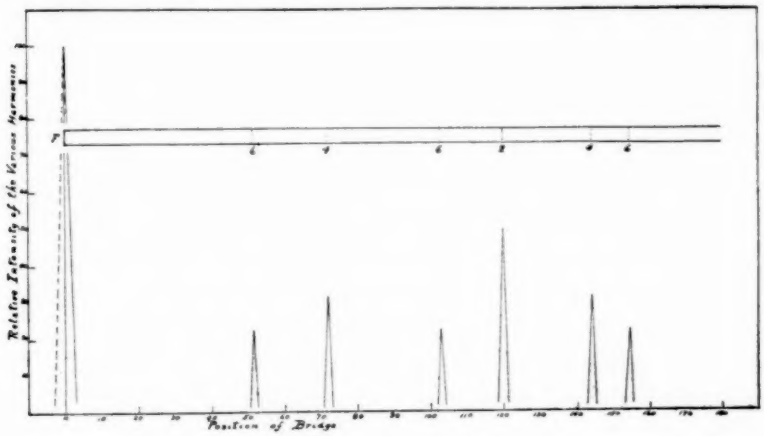

Fig. 4*a*.

Ratio of frequencies 1 : 3 : 5 : 7.
Ratio of intensities 1 : 0.50 : 0.31 : 0.22.

This curve gives us the clue to the explanation of Curve *II*. The numbered maxima in the two curves correspond. In making a comparison it should be borne in mind that the total wire system for Curve *II* was several centimeters longer than for Curve *III*. In *II* undoubtedly the maxima marked *XXX* and *YYY* are due to the oscillator. In figuring the internodal space for the *X* and *Y* maxima, the work of Blake and Sheard[1] will show that the *X* and *Y* maxima at 142 and 150 respectively are influenced by the free overtone marked 6 at 146 and vice versa, and so only the other maxima are used. This gives the half wave length for the *X* oscillation as 67 cm. and for the *Y* oscillation 51 cm. An inspection of the figure will show that the *Y* maximum is some greater in intensity than the *X* maximum, though not much greater (10 per cent.). It is to be remarked, however, that in general for all the

[1] See note, page 474.

curves shown in this paper there seems to be a general tendency for the maxima quite near the oscillator end to be smaller than the others due to some action not yet clear, and hence since the X maximum at 11 is so much closer to the oscillator than the Y maximum at 48 one can safely say that the X and Y maxima are equal in intensity. These maxima will be spoken of again.

Having ascertained under what conditions practically only the free vibrations of the Lecher system were present it became of interest, as already stated, to ascertain how the wave system was affected by a change in the length of the air-gap. Accordingly, setting the oil-gap length at a certain constant value before each curve was taken and starting with each column of water resistance 30 cm. long, a series of curves was taken with different lengths of air-gap. Seven such curves were taken but to avoid confusion in the figure only four are shown in Fig. 5. It is seen at once that there is not even a slight displacement of any of the maxima as the air-gap is lengthened or shortened. The curves of this figure are recalculated to open circuit on the galvanometer variable shunt. Specifications for the different curves of this paper are collected

TABLE I.

Specification.		Length of Air-gap in mm.	Length of Oil-gap in mm.	Length of Water-resistance in cm.	Condenser (C, Fig. 3).
No. of Fig.	No. of Curve.				
2	I	0	?		
2	II	2 about	?		
2	III	1.53	0.10	30	Inserted.
5	I	1.30	0.10	30	Inserted.
5	II	0.64	0.10	30	Inserted.
5	III	0.31	0.10	30	Inserted.
5	IV	0.13	0.10	30	Inserted.
5	V	0	0.10	30	Inserted.
5	VI	0	0.10	30	Inserted.
8		1.22	0.10	30	Inserted.
11	I	1.22	0.10	0	Removed.
11	II	1.22	0.10	0	Inserted.
11	III	1.22	0.10	30	Removed.

together into Table I. The three curves taken but not shown lie in between the others. Plainly as the air-gap is lessened the size

of a reading for a given bridge position increases up to a certain point, but the ratios between maxima and minima decrease to a marked extent. This means, we think, that more and more energy overflows from the induction coil past the oscillator on to the Lecher wires, thus always giving a fairly large potential difference at the bolometer end of the wires no matter what the bridge position. An explanation of such action is perhaps afforded by thinking of the whole system from the secondary terminals of the induction coil clear through the oscillator to the free end of the Lecher wires as a single swinging system with inductance and capacity. The action with the Blondlot oscillator with primary and secondary very close together and with no air-gaps present can be thought of as similar to that with the Lecher oscillator with the primary and secondary plates very close, when instead of two separately swinging systems there is but one.[1] With but a single system one cannot expect the potential difference at the end capacity to change much as a bridge is moved along over a part of that system. If we have air-gaps present, however, then the short oscillator system may be said to set the longer Lecher system into vibration and as the air-gap is increased in length the more independent does the Lecher system become both of the "slopping-over" of energy from the induction coil and of the forced vibrations of the oscillator.

A study of the curves of Fig. 5 together with Curve *III* of Fig. 2 and two or three others already spoken of but not shown shows the more important maxima to be located at the positions given below. A second bridge showed what maxima responded and although it was found that the use of a second bridge invariably displaced the maximum toward the oscillator end thus shortening the internodal space, still the displacement was always small and hence there can be no question as to what maxima belong together. The strongest maximum occurred at 111.3 cm., the next two at 134.7 and 60.7, the next three at 35.2, 89.7 and 144.3 cm. These figures are accurate to within 2 mm., obtained as the mean of all the curves on the assumption of no displacement due to shortening the air-gaps. It was found experimentally that the deflection for no bridge compared to that for a single bridge at the 111.3 cm.

[1] See Drude, Wied. Ann., p. 632, 1897.

maximum was 2.5[1] times as great and it became at once apparent that we have here a first approximation to the system shown in Fig. 4*a*. It was evident, however, that it was only an approximation as the following calculation shows. The end of the Lecher wires (flush with the outer end of the small Leyden jars) was 165.0 cm.

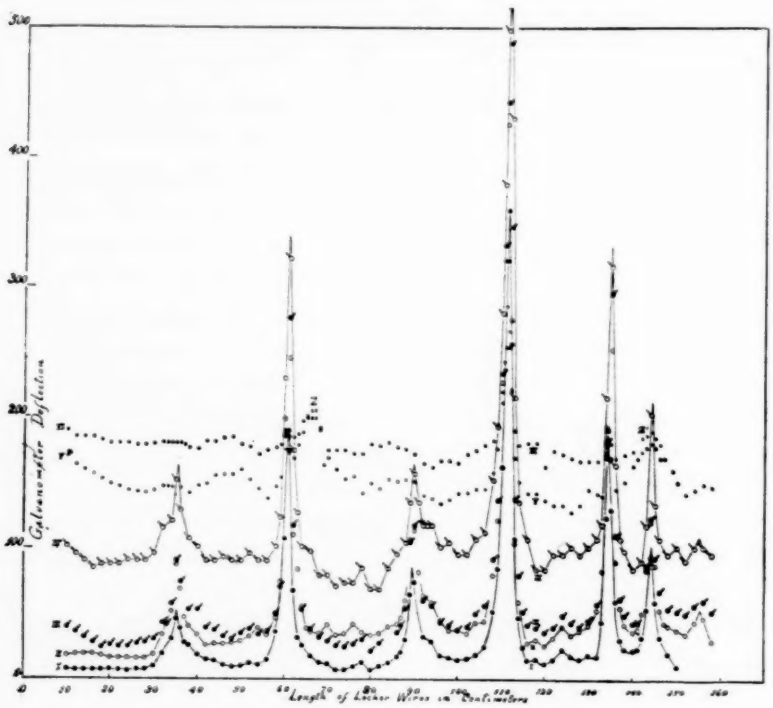

Fig. 5.

The internodal space for the maxima at 134.7 and 60.7 is 74.0. Multiplying this by 10 gives for the fundamental wave-length 740 cm. Also, the three other maxima above give 764 cm. for the fundamental wave-length. Furthermore, using these two overtones for calculating the end of the Lecher wire including the end-capacity we obtain 171.6 cm. (*e. g.*, 134.7 + ½ of 74 = 171.7). Subtracting 111.3 from 171.6 gives 60.3. Multiplying by 12 gives 723.6 as the

[1] For all the curves this ratio never differed more than 4 per cent. from 2.5. The mean of all was just 2.50. However when the air-gaps were very small this ratio decreased until for zero air-gap it was only 1.3.

fundamental wave-length, λ_0. If the ideal case pictured in Figs. 4 and 4*a* were experimentally obtained these numbers for λ_0 should be identical. Plotting these numbers against the corresponding frequencies gives the curve shown as *I*, Fig. 6. Extrapolating the

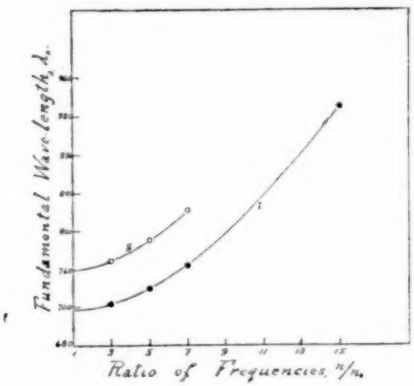

Fig. 6.

curve we obtain for the true fundamental wave-length 713 cm. Similarly from Curve *II* of Fig. 2 we obtain Curve *II* of Fig. 6, giving 760 as the extrapolated fundamental wave-length. Assuming the internodal spaces all equal for any given tone of the curves of Fig. 5 we obtain for the location of the node at the oscillator end these figures for the sixth, fourth, second harmonics and fundamental respectively, − 19.5, − 13.3, − 9.3, − 6.6 cm. Now the points XX' of the secondary (Fig. 1) were located at − 6.7 cm. while the point k (measured along the circumference) had the position of − 14.5 cm. This argues strongly that the electrical vibrations for the fundamental tone at least does not follow along the circumference of the secondary but jumps across the neck of the secondary at XX' (Fig. 1).[1] For this reason it seems as if it would be better to have the spark-gap of the oscillator at k rather than at a, although Drude[2] objects to this arrangement.

[1] In another paper by Blake and Sheard it will be shown that the fact that λ_0 obtained from the overtones increases with the frequency is due to the reaction of the oscillator upon the Lecher system on account of the closeness of the coupling. When the coupling is very loose it is found that the overtones are strictly harmonic. See note at bottom of page 474.

[2] Drude, *loc. cit.*

An attempt was made to classify the less intense overtones of the curves *I–IV* of Fig. 5 and Curve *III* of Fig. 2, though not with much success perhaps. Secondary maxima common to all these curves occur at 32, 39, 52, 63, 78, 94, 104, 125 and 156 cm. in round numbers. It would seem that the maxima at 32, 63, 94, 125, 156 belong together, for the common internodal space is 31 cm. (= 2 (171.6 − 156)). They probably belong to the seventh overtone (*i. e.*, the fourteenth harmonic modified by the close coupling). On this basis the seventh overtone is to be seen in Curve *I* of Fig. 6. A discussion of the remaining secondary maxima at 39, 52, 78 and 104 cm. cannot be given till later. Curves *V* and *VI* were taken with zero[1] air-gap length and should duplicate each other, a thing they do as to *type* certainly. For all the curves of Fig. 5 the actual observations are given uncorrected for oscillator deterioration and since for zero air-gap the spark was more disruptive than usual the duplication is sufficiently satisfactory, especially when the crudeness of the method for measuring the oil-gap and air-gaps is remembered.

An appreciation of the effect of the air-gap length upon the vibrating system in the Lecher wires can be gained from Fig. 7, obtained indirectly from Fig. 5 by getting the ratio of the first overtone maximum at 111.3 cm. to the mean minimum at 18 to 26 cm. inclusive. We say "indirectly," for in Fig. 7 the oscillator

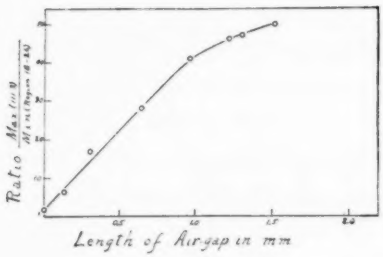

Fig. 7.

deterioration has been corrected for as far as possible. Moreover, the results of curves not shown are included in Fig. 7. For the largest air-gaps obtainable with the induction coils[2] at our disposal

[1] After closing the gaps by pushing the balls *ff'* against *ee'* fine copper wire was soldered across each gap back of the balls.

[2] It should be borne in mind that they were operated without condenser or interrupter.

a ratio of 50 to 1 was obtained. Still larger air-gaps would have given a somewhat larger ratio. The relation between this ratio and the length of air-gap is seen to be a linear one up to 1 mm. length. Beyond that an increase of air-gap length has less effect. By a rough extrapolation one could say that a ratio of 60 to 1 could be obtained for a 3-mm. air-gap.

Since it has been proven that the oscillator was able at times to force some of its own vibrations upon the Lecher system it seemed worth while to try to see if some of the secondary maxima of curves *I–IV* of Fig. 5 might not be attributed to the oscillator. They were too feeble, we thought, to make the method of responses by employing additional bridges seem satisfactory when we knew that each additional bridge displaced its maximum somewhat, the effect being cumulative. It seemed wiser to search for resonance between the oscillator and Lecher system by employing no bridge and shortening the Lecher system. Starting with the length 165 we cut off 2 cm. at a time down to 45 cm., taking three readings of the galvanometer after each cut. The results are shown as circles (O) in Fig. 8. Continuing this work we thought we were bothered with difficulties due to the tension[1] of the Lecher wires changing. Accordingly, in order to apply a large known tension a loop of wire was soldered to each Lecher wire back of the Leyden jar and a cord ran from this loop over a pulley to a scale pan carrying 2.5 kilos. This variation rendered the work of shortening the Lecher system much more tedious and proved unwise in the end. For by reason of the increase in the time necessary to run a curve it probably introduced more error than was eliminated by the assurance of a constant tension. Nevertheless it was persisted in and many curves and parts of curves were taken for longer and shorter Lecher systems. The observations are all plotted in Fig. 8, each new symbol displayed in the figure showing a new wire system that was cut. The curves indicated by the various symbols ought to be compared as to type more particularly, for the actual value of the ordinate for any given abscissa is dependent upon several factors, more particularly oscillator deterioration, over which we had no control; and hence we could not make the curves shown by the

[1] Up to this time the wires were held taut by wooden plugs driven into a wooden support.

various symbols directly comparable except in a qualitative way. However, each set of symbols, in so far as it goes, shows various maxima and minima, so that taking all the symbols together and averaging, a curve can be drawn about as shown in the figure,

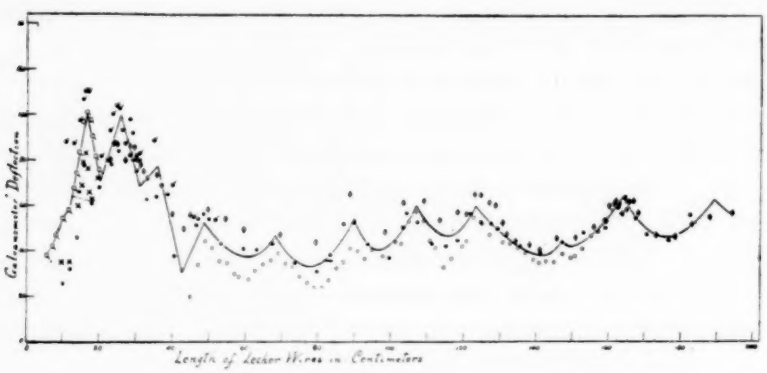

Fig. 8.

each maximum being accurate within 2 cm. at most. If more faith be put in the circles (○) as having been obtained under the best conditions, one could say that the maxima and minima are about equally sharp, the curve having the maxima purposely somewhat too sharp. Two strong maxima of equal intensity are seen at 16 and 26, close to the oscillator, with other maxima, but less strong at 49, 68, 90, 107, 123, 164, 189, enough points not having been taken definitely to locate the last one. Secondary maxima are seen at 10, 36 and 147.

We believe we correctly interpret Fig. 8 as follows: The two maxima at 16 and 26 represent the *two* lengths of the Lecher system that respond to the vibrator because of the closeness of the coupling.[1] Choosing the maxima 26, 68, 107, 147, and 189 one may call the common interval 41 cm., giving as the wave-length 82 cm. With the other maxima 16, 49, 90, 123, 164 it is seen that the interval is either 33 or 41. These figures of 66 and 82 cm. as the two fundamental oscillator wave-lengths are confirmed in two ways. Their mean, 74.2 cm., calculated[2] from $T_1^2 = T^2 + \theta^2$ and

[1] See A. Oberbeck, Ann. d. Phys., Vol. 55, p. 624, 1895, or Fleming, Principles of Wireless Telegraphy, p. 209, first edition.

[2] See Fleming, *loc. cit.*

$T_2^2 = T^2 - \theta^2$ agrees with Coolidge's value of 74 cm. for a Blondlot oscillator of 5 cm. diameter. Moreover, if one figures back to the point k of the oscillator he obtains the same values for the half wave-lengths thus: the wires leading from the Lecher Leyden jars to the bolometer were 1 cm. from the outer end of the jars, an amount to be subtracted from the maximum position. The distance from the arbitrary zero to the petroleum free surface was 6 cm., while the length of the secondary under the oil up to k (Fig. 1) was 8 cm. We have then, $15 + 6 + 8 \times 1.43$ (index of refraction of petroleum) $= 32.5$. Similarly, $25 + 6 + 8 \times 1.43 = 42.5$ cm., thus giving numbers in substantial agreement with those obtained above. In the same way we get 26.5 cm. for the secondary maximum at 10 and 36.5, though beyond that on the Lecher system this sub-multiple of the oscillator seems too weak to detect. Since $82/53 = 3/2$ it would seem that this weak oscillation is the upper fifth of the longer of the two oscillator fundamentals. It would appear now that the unexplained secondary maxima of Fig. 5 at 52, 78 and 104 cm. are due to this vibration of the oscillator.

Now Curve *II* of Fig. 2 was taken with an oscillator[1] other than the one used for most of the curves of this paper. In the light of the presence of two fundamental vibrations of equal intensity, one higher in frequency, the other practically the same amount lower than the true fundamental tone of the oscillator, it seems likely that the maxima X and Y of Curve *II*, Fig. 2 represent these two fundamental tones. If it be objected that the one circuit was much longer than the other and hence that the conditions were not right for producing two fundamental tones of different period, let the reader remember that we are here dealing with *forced* oscillations.

The maximum marked Z at 66 cm. in Curves V and *VI* of Fig. 5 we are unable to interpret. It has begun to show itself in Curve *IV* of the same figure. We think it has a counterpart or corresponding maximum Z' concealed somewhere between 140 and 150, for Curve V shows the maximum at 144 to be too broad at the base to contain only the maximum due to the third free overtone at 144.3. Moreover, the other points for this third overtone are seen to be prac-

[1] Its true dimensions are not now available.

tically absent at 35 and 90 in Curves *V* and *VI*, which would strengthen this idea. Calling $Z' = 142$ we thus get the internode 76 cm., or the wave-length 152 cm., a little more than twice the true fundamental of the oscillator. On this view it would seem that for no air-gaps in the vibrator circuit a portion of the lead wires form a part of the oscillating circuit, whereas when suitable air-gaps are used not even the wires *mm'* (Fig. 1) take part in the oscillation.

Keeping the air-gaps constant at 1 mm. length (accurately 0.94 mm.) we tried the effect of changing the length of the oil-gap. The Lecher circuit was somewhat longer than 165 cm., for the first overtone maximum was at 113 instead of 111.3 cm. The results obtained are plotted in Fig. 9. A glance at Curve *III*, Fig.

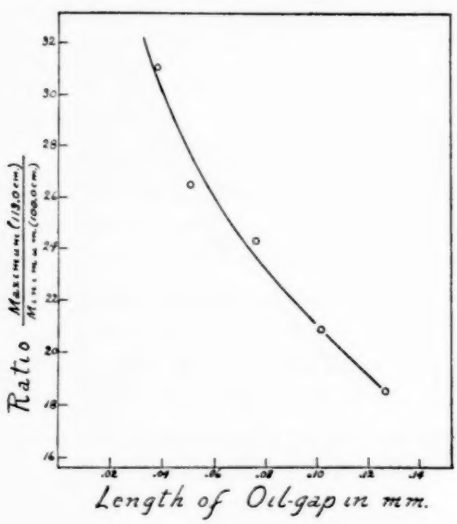

Fig. 9.

11, shows that a minimum occurs at 100, and so, instead of taking full curves, alternate readings were taken at 113 and 100, usually seven in number. Necessarily the true location of the curve of Fig. 9 was by far the most difficult of all the curves to obtain. The thickness gauge was used to measure the length of oil-gap and at best the method is exceedingly inaccurate. Fig. 9 is the mean result of four trials; in three of these the oil-gap was first increased

and then decreased by steps. There can be no doubt of the general nature of the curve. The minimum limit of the gauge was 0.0015 inch, so still smaller lengths than shown could not be investigated. While undoubtedly the smaller oil-gaps gave better ratio values, nevertheless for them the oscillator was much less steady in its action, so that in general we preferred to work with a gap 0.1 mm. long.

In the same way we tried the effect of changing the length of the water resistance back of the oscillator and the results are shown in Fig. 10. Here again the curve is the mean of several trials,

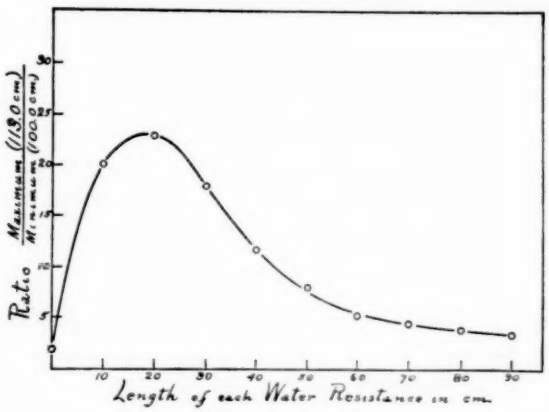

Fig. 10.

first increasing and then decreasing the length. For a length below 20 cm. for each water column the spark became so snappy and disruptive as to render the oscillator action unsteady. Accordingly we cannot say that the maximum at 20 cm. is correct to within 5 cm. either way. For the sake of steadiness of action 30 cm. was chosen in most of the work of this paper.

Then we tried the effect of making the water resistance zero. But the spark gap at once became too disruptive to work with so we removed the condenser also (*C*, Fig. 3). As a result we obtained Curve *I*, Fig. 11. It was at once evident that the free vibrations of the Lecher system were the only vibrations present and they were *exceedingly feeble.* Then to see whether this great change in the character of the wave system was due to the condenser or to

the absence of water resistance we again inserted the condenser. But we had proceeded with the curve (*II*, Fig. 11) only 50 cm. along the wires when the mica insulation between the primary and secondary of the oscillator was punctured by the spark and hence

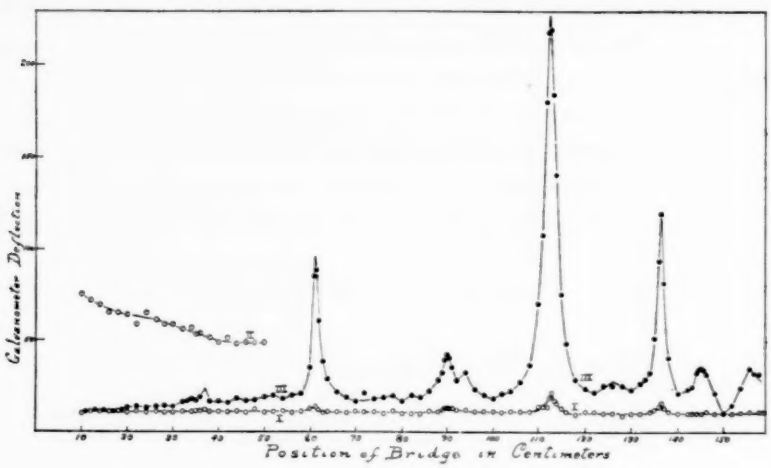

Fig. 11.

we didn't try to proceed. However, there is no evidence of the maximum at 37 and so we concluded that the introduction of the free vibrations to any marked extent must have been due to the presence of the water resistance. We then proceeded to confirm this view by running a curve with a 30-cm. water resistance but without the condenser. Thus we obtained Curve *III*, Fig. 11. Its similarity to many of the other curves shown is at once apparent.

CRITICAL DISCUSSION.

We have shown by the results here presented that there are two very necessary conditions that have to be fulfilled before the free vibrations of the Lecher system are able to establish themselves in all their simplicity (except as they are influenced by the closeness of the coupling of the oscillator system). These two conditions are the introduction of water resistance back of the oscillator and in the same place but nearer the oscillator two symmetrical air-gaps. We have tried in the curves of Fig. 5 to show the functioning of the air-gaps and in those of Figs. 10 and 11 that of the water

resistance. The point on the Y axis of Fig. 10 is obtained of course from Fig. 11. Unquestionably, the general nature of the curve of Fig. 10 is right, but the difficulties under which it was obtained were great and the number of points in the region of short lengths were too few to locate it accurately. It is hoped in a later report to be able to discuss more intelligently than is now possible the exact functioning of the water resistance in such work. The importance of the fulfilling of the above conditions will, we believe, be at once recognized.

We surmise it must have long been a source of wonder to many an experimenter why the curves of Rubens,[1] which undoubtedly represent the free vibrations of the Lecher system, had relative intensities for the different tones so at variance with what one might expect from a knowledge of acoustical vibrations. We hope this paper may help to clear up the matter. It would appear that it is necessary to prevent the free vibrations from being swamped by those of the induction coil and oscillator lead wires, and that the introduction of water resistance and air-gap resistance affords the necessary prevention.

It becomes interesting then in the light of such investigations to see in how far the above results lend themselves to known theories, particularly to that developed in essence by Kirchhoff[2] and in full detail by Abraham.[3] Employing the latter's notation we have for the potential difference $\Phi_1 - \Phi_2$ between the wires

$$\Phi_1 - \Phi_2 = \frac{2|A|}{K} \cos\left(\frac{\nu x}{w} - \gamma\right) \cos \nu t,$$

and for the current

$$J_1 - J_2 = w \cdot 2|A| \sin\left(\frac{\nu x}{w} - \gamma\right) \sin \nu t,$$

where x is the distance measured along the wires, K the capacity of the wires per unit length and γ the half phase change upon reflection from the free end of the wires due to end-capacity (the detecting Leyden jars). If a bridge is employed, there is of course

[1] Rubens, *loc. cit.*

[2] Kirchhoff, Pogg. Ann., 121, p. 551, 1864.

[3] Abraham, *loc. cit.*

a node of potential difference at the bridge. The above equations express the possible free vibrations of the Leyden jars when connected by the parallel wires and the bridge. Take the end capacity at $x = 0$ and the bridge position at $x = -l$, then for a given frequency ν, the values of l where potential nodes should be found are determined from the equation

$$-\frac{2\pi l}{\lambda} - \gamma = -\frac{\pi}{2} + m\pi,$$

where $\tan \gamma = 2\pi K_0/\lambda K$, w being the velocity of free radiation and m a whole number. On the other hand if the length of the wires is given reckoned from the bridge position to the end-capacity, the frequency of the possible free vibrations is determined from the transcendental equation $\xi \tan \xi = \alpha$ where $\xi = 2\pi l/\lambda$ and $\alpha = Kl/K_0$. Now the end of the wires was at 165 cm. and the wire end including end-capacity was shown above to be 171.6, giving $K_0 = 6.6K$. Extrapolating the fundamental wave-length from Fig. 6 to be 712.8 and using this value throughout we get the results indicated in Table II. with the percentage error shown in column 8, assuming

TABLE II.

No. of Overtone.	Observed x.	λ	$\xi \tan \xi$	λ' from Fig. 6.	$\xi' \tan \xi'$	α	Per Cent. Error $\frac{\xi \tan \xi - \alpha}{\alpha}$.	Per Cent. Error $\frac{\xi' \tan \xi' - \alpha}{\alpha}$.
0								
Fund.	171.6	712.8	26.00	712.8	26.00	26.00	[1]	
1	53.7	237.6	9.34	241.2	8.05	8.14	+ 14.8	− 1.1
2	30.3	142.5	5.55	148.0	4.38	4.59	+ 20.4	− 4.6
3	20.7	101.8	4.25	109.1	3.01	3.14	+ 35.4	− 4.1
7	9.0	47.5	2.98	62.0	1.19	1.36	+119.0	−12.5

α correct. It is evident at once from the table that the theory is far from being satisfied. If on the other hand one uses instead of λ in the formula a value λ' obtained from Fig. 6, the agreement may be said to be quite satisfactory. It is so good in fact that one is safe in saying that to a first approximation the effect of the close coupling is one of increasing the wave-length of the overtones and the higher the tone the greater the effect. This confirms the viewpoint gained in drawing the curve of Fig. 6.

The result of a comparison of theory with experiment as to the

[1] $\xi \tan \xi$ was put equal to α here in order to extrapolate the value of λ_0.

relative intensities of the various maxima is summed up in Table III. The relative theoretical value of any maximum is equal to

TABLE III.

No. of Overtone.	$\sin\left(\frac{\pi}{2}\cdot\frac{1}{2N+1}-2\gamma\right)$.	Relative Intensity (Fund. = 100 Per Cent.)	$\sin\left(\frac{\pi}{2}\cdot\frac{1}{2N+1}-2\gamma'\right)$.	Relative Intensity.	Observed Intensity.
0 Fund.	0.994	100.0	0.994	100.0	100
1	0.397	39.8	0.399	40.0	40
2	0.197	19.8	0.193	19.4	20
3	0.108	10.9	0.100	10.0	9
7	−0.012	−1.2	0.016	1.6	2

$$\sin\left(\frac{\pi}{2}\cdot\frac{1}{2n+1}-2\gamma\right)$$

where n is the number of the overtone and 2γ is the phase change on reflection due to the end-capacity. Now

$$\gamma=\tan^{-1}\frac{2\pi}{\lambda_0}\frac{K_0}{K}$$

and hence is 3° 19′ 50″. From Table III. it is seen that the intensity of the seventh overtone has a negative sign which shows that the close coupling of oscillator and Lecher system plays another part besides that of changing the wave-length already mentioned. If one introduces γ' for γ where

$$\gamma'=\gamma\frac{\lambda_0}{\lambda'},$$

the seventh overtone comes out positive. Now it is evident for weaker overtones that the average minimum of the curve should be subtracted from the average observed deflection for a given overtone before a fair comparison can be made. It will be observed from the curves that there is a general tendency for the minima to increase in intensity as also the maxima as their distance from the oscillator increases. It is clear, moreover, that when a maximum belonging to a given overtone occurs on the slope of a maximum of another and stronger overtone, this fact must be taken into account in estimating the mean value of the maxima for that overtone. Attempting such corrections for all the curves taken which have proper water resistance and air-gap we obtain the figures shown in the sixth column of Table III. A glance at any

of the curves will convince one of the substantial correctness of the figures there shown. From Tables II. and III. the agreement between the theory, modified because of close coupling, and experiment may be said to be quite satisfactory.

After the presentation of these results it would seem wise, perhaps, to enter into a critical discussion of the results of other experimenters. To avoid repetition it seems best, however, to defer such discussion until after the results of Blake and Sheard[1] are presented and these will follow in due course.

In closing this paper only one other thing need be pointed out. The ever-present question of the proper relation between wire-length and wave-length is still unsettled.[2] These experiments throw some light on the question we think. We confess to some surprise that in comparing theory (modified) and experiment we found it necessary to use the outer end (away from the oscillator) of the Leyden jars rather than their inner end in calculating the phase change. Rather, perhaps, can we more safely say that the free end of the wire had to be used. This gives us $K_0 = 6.6K$. Now the actual wire-length of the Lecher system was 2 (165.0 + 6.6) up to the neck XX' of the secondary giving 343.2 cm., neglecting the distance XX' across the neck.[3] Dividing this into 712.8, the extrapolated value for λ_0, we obtain 2.08. If we include the neck this ratio becomes 2.07. We interpret the fact that in estimating γ, the free end of the wire has to be used to mean that the theoretical value of 2.00 obtained by Poincaré, Abraham and others can never be obtained in practice. Just as in acoustics there is always an "end correction" for resounding air-columns so in electricity there is a corresponding end correction which is *always* present. One might say that the very momentum of the electric wave carries it *beyond* the end of the wire before reflection occurs. It is seen, then, that the value of the end correction is say at most 4 per cent. If

[1] The experiments described in this paper were performed in 1907–8, but for various reasons their publication has been deferred. In the meantime the results obtained by Blake and Sheard have become known to the writers. Their results have largely influenced the point of view of this paper, especially in regard to the influence of the oscillator coupling upon the results enabling us to point out the way in which Abraham's theory of free oscillations must be modified to fit the facts for a closely coupled circuit. It is with pleasure that we acknowledge all credit due them in this and other regards.

[2] See for instance an article by Ives in PHYS. REV., September, 1910.

[3] As a matter of fact XX' was somewhat less than 2 cm., say 1.5 cm.

the *entire* length of the secondary were added to the Lecher system the total metallic circuit would be 359 and if the value of λ_0 were extrapolated as high as 718 this would give exactly 2 for the above ratio. This cannot possibly be right, however, as the work of Blake and Sheard will later show. A value as high as 718 is impossible from Fig. 6, moreover.

The theoretical value of 2.00 makes no allowance for the end correction. Assuming for the moment its entire absence we may say that the Poincaré-Abraham value of 2.00 holds, *but for a non-radiant system.* In this connection it is interesting to note that the recent values obtained by Ives vary from 2.03 to 2.08, for a system also *non-radiant*, though for an entirely different reason.

Summary.

It has been shown in this paper how it is possible to obtain on a set of parallel Lecher wires a system of free vibrations uncontaminated by oscillator influence except that of coupling. It was found that the unmodified theory fitted even the case of close coupling to a first approximation. The manner in which the theory has to be modified for a second approximation was pointed out. The conditions for freedom from contamination were found to be two, the introduction of suitable air-gaps into the oscillator circuit and suitable water-resistance between the induction coil and oscillator. The results of varying these conditions were studied. A ratio between fundamental maximum and minimum equal to 125 to 1 was experimentally obtained and it was thought that this ratio could be materially increased by observing the best conditions for controlling the various factors that enter into the problem. The ratio between Lecher wire-length and wave-length was found to be 2.07 and the difference between this value and the theoretical value 2.00 was shown to be due to an "end-correction" which is necessarily always present.

In the earlier part of the paper where the Wehnelt interrupter was employed the work was done by one [1] of us under the supervision of Professor A. D. Cole and we take pleasure in expressing our best thanks to him for his suggestions and advice.

Physical Laboratory,
Ohio State University.

[1] Miss Ruppersberg.

ON THE RELATION BETWEEN THE DENSITY AND CONCENTRATION OF AQUEOUS SOLUTIONS.

BY PAUL FREDERICK GAEHR.

IN the winter of 1907–8, in connection with an experiment to determine the curve between the density and concentration of a solution of common salt, a very simple equation was found. I then set out to see if this equation is also good for the solutions of other salts, and of acids.

The proposed equation is

$$\log \delta = mc,$$

wherein δ = density and c = concentration. This simple equation was first found for solutions of common salt. I had attempted to derive an equation based on the following assumption. Let V be the specific volume of a solution of concentration c per cent. Then in 1 gram of the solution are contained $c/100$ grams of the salt, and $(100-c)/100$ grams of water. If on mixing these, the sum of their individual volumes is equal to the specific volume, we have a very simple case. Unfortunately, the facts are otherwise. If we represent the density of the salt by s, and the density of water by w, and the sum of the individual volumes of salt and water v, then we can write

$$v = \frac{c}{100s} + \frac{100 - c}{100w}.$$

Now if there were a simple relation between v and V like $V = mv + n$, wherein m and n are constants, we would be led to a linear relation between V and c. But such was not the case with NaCl.

Now in the case of no "shrinkage," *i. e.*, where $V = v$, we should have

$$V = \left(\frac{1}{s} - \frac{1}{w}\right)\frac{c}{100} + \frac{1}{w}.$$

So I plotted this line. The difference between corresponding

ordinates of this and the preceding curve represent the "shrinkage" and I had hoped that perhaps this could be more easily handled. It then occurred to me that the curve between V and c very much

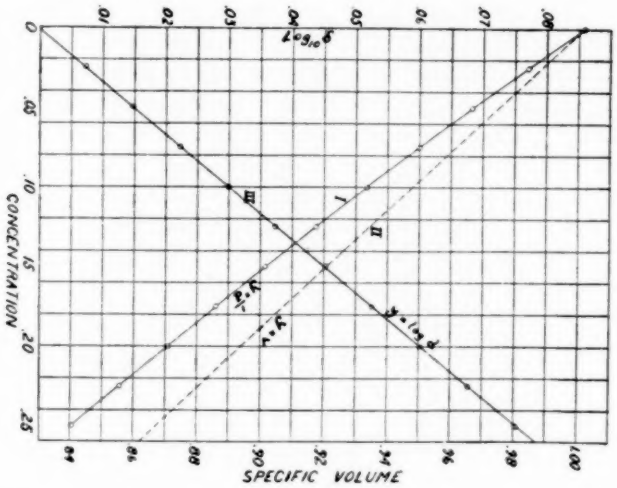

Fig. 1.

resembled a "decay-curve." I found that equally spaced ordinates formed a geometric progression, my conjecture thus proving true. Therefore I knew that the equation must be $V = 10^{-mc}$ or $1/V = 10^{mc}$.

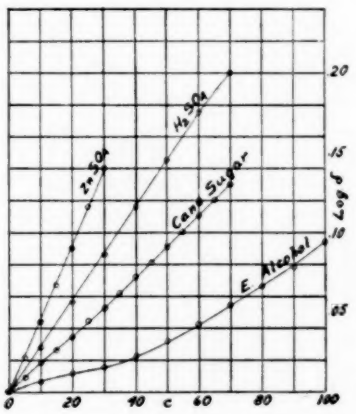

Fig. 2.

Hence $\log \delta = mc$. The reason for choosing 10 as the base of the exponential is thus apparent. The reason for not multiplying the

exponential by a constant is that $\delta = 1$ when $c = 0$. The justification

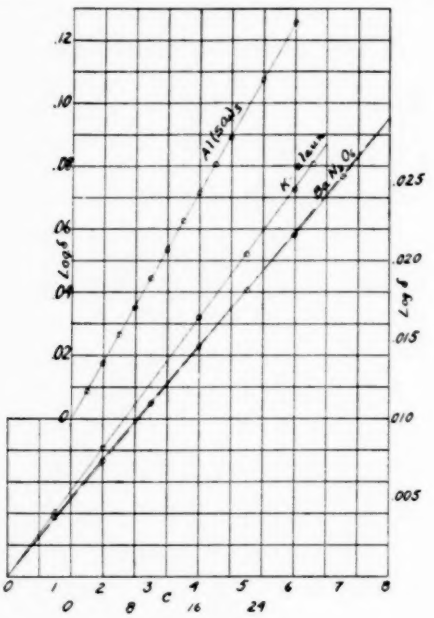

Fig. 3.

for this equation as applied to solutions of NaCl will be found in Fig. 1.

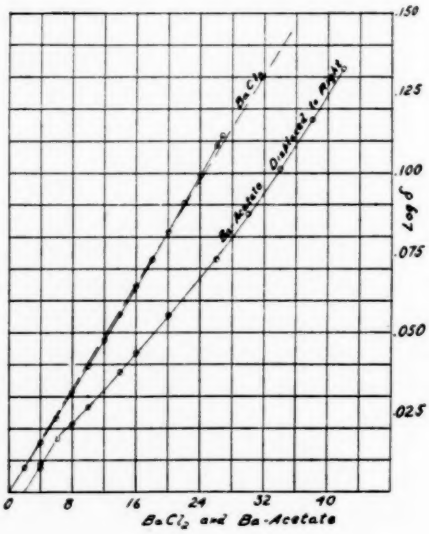

Fig. 4.

This equation was tried for a number of other salts, and also for some acids (see Fig. 2). To some it applied, to others not. It seemed worth while however to make an inventory of the inorganic

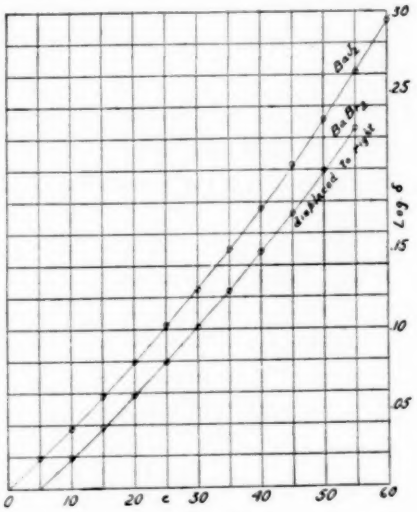

Fig. 5.

salts to begin with, to see if it might be possible to settle any one of these points: (1) Do the salts that obey, obey also some other common law, or have they some common properties? (2) Are

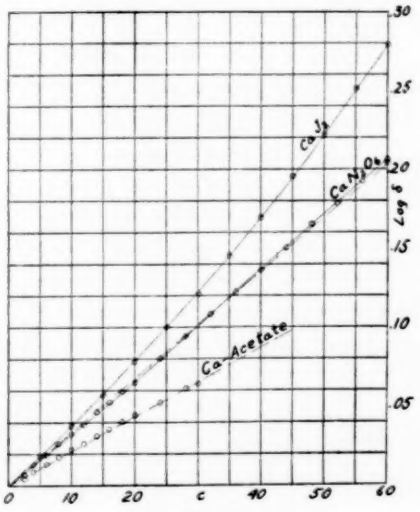

Fig. 6.

the slopes related to the atomic weight so as to be easily computed from them? (3) Can the deviations from the law proposed above be explained on any ground? (4) Does the law throw any light on the molecular behavior of those salts that obey it? I have attempted no answers to any of these questions, but have confined myself to a statement of facts, largely because I was unable to finish the list of salts. The data for the curves were taken partly from Landolt and Boernstein, partly from Kohlrausch's Handbuch der Praktischen Physik, and partly from the Chemiker Kalender for 1908.

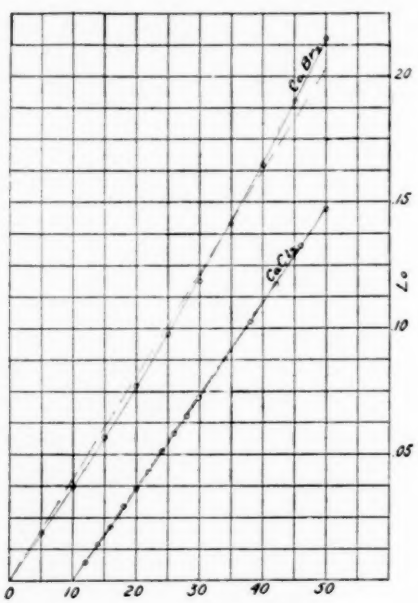

Fig. 7.

In the last named book I found a few typographical errors, which led me to suspect, when a bad irregularity occurred, that I had an error before me. So a few salts were dropped for that reason. Also, I soon discovered that when a curve is short, it is straight; so salts whose saturation came at concentrations less than 20 per cent. were dropped.

There are three general classes of curves to be found:

(*a*) Straight lines; this includes those curves which differ but little from a straight line. The criterion for this was that the

density as taken from the curve should at no point differ from the density as taken from the average straight line by more than 1.2 part in two hundred, *i. e.*, by not more than six tenths per cent.

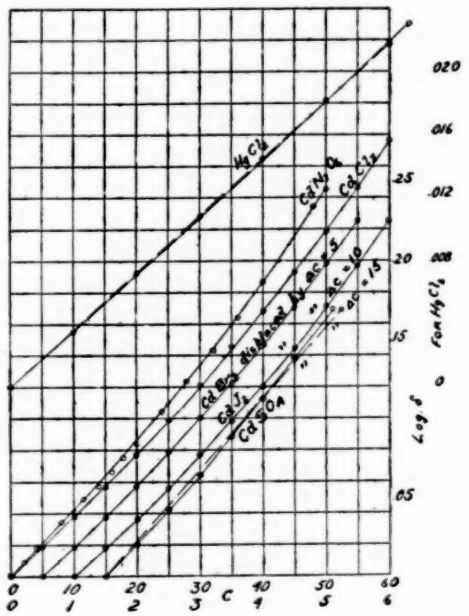

Fig. 8.

(*b*) Curves sloping uniformly upward or uniformly downward.

(*c*) Curves with double curvature.

The easiest way to test the applicability of the law was to plot values of c in per cent. as abscissæ, and corresponding logarithms of the density as ordinates. The average slope was computed from the data, according to the formula: slope = (sum of ordinates) divided by (sum of abscissæ). The least square formula for the case that the y-intercept is equal to zero reduces to this. It were better to say that the curves of class (*b*) were concave or convex toward the x-axis. A few among class (*b*), and more among the third class, exhibited the peculiar phenomenon of being perfectly straight over a considerable length.

In view of this fact, especially, and also of the double curvatures, it must be evident that the fitting of a single equation to all salts

is not an easy matter. We might have tried to fit a parabola of the nth order to the curves, and have said that in the case of certain salts the coefficients of the x's are such as to make it the series for 10^{mc}. However the computation of the coefficients is apt to be a very long task, and in the cases of some salts, whose densities are given only to the third decimal place, next to impossible. Besides this, there is a very good reason for sticking to the logarithmic equation, for differentiation gives

$$\frac{d\delta}{\delta} = \frac{m \cdot dc}{\log_{10} \epsilon},$$

an equation whose significance will be pointed out later.

At this time it may be useful to recall how the tables of densities are made up. As a rule, the observer did not have precisely 5,

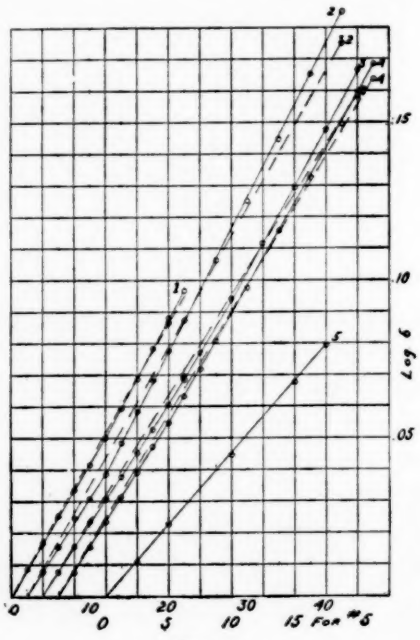

Fig. 9.

10, 15, etc., per cent. He made up his solutions as near these values as possible, plotted a curve, and then by interpolation got the values for the concentrations given in the table. Or else, the observer

might find the densities corresponding to certain degrees on, say, the Beaumé hydrometer, and the compiler of tables then does the interpolating. That this may lead to errors of greater or less magnitude must be clear.

It is difficult to believe that men whose data are quoted in such works of compilation as Landolt and Boernstein's, should have omitted any precautions in their measurements. Yet the writer

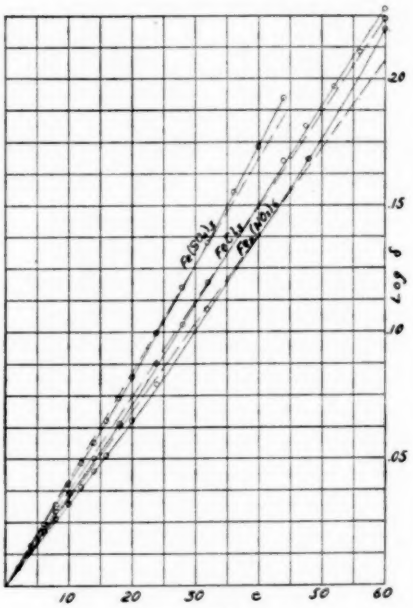

Fig. 10.

ventures to suggest that perhaps some unknown error was committed which in the case of certain salts varies with the concentration.

In the diagrams presented in this paper, I have in some cases, to prevent the overlapping, displaced curves to the right or upward. Remembering that the log of the density is zero for zero concentration, one easily finds the origin for each curve; the coördinates of any point on the curve must then be corrected for the displacement. The straight lines drawn with the curves represent the line of average slope, the computation of the slope being performed as explained on a preceding page.

In the tables, the salts are arranged in accordance with the curva-

ture as indicated on a previous page. For the salts of class *A*, I have also tabulated the molecular weights, the slopes, and the maximum relative error (in per cents) made made by taking the calculated density instead of that found in the tables. This per cent. error was not calculated for all the salts; where a curve deviated considerably from a straight line, or else not noticeably, the error was not calculated. There is given for all the solutions the maximum density and the corresponding concentration.

It was stated above that several curves contained straight segments. Such are marked by an *s* in the last column. Those curves whose error is so small as to admit them into class *A*, but which nevertheless show a clear deviation from the straight line, are marked by a *b* or *c* in the fifth column. It is remarkable how cadmium

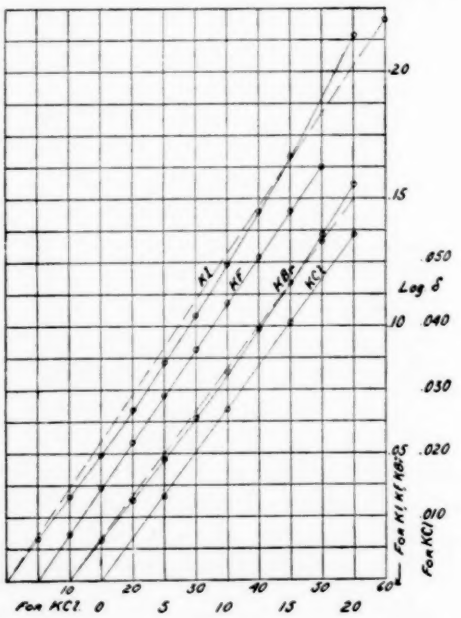

Fig. 11.

nitrate and barium acetate show an irregularity near the origin. Alcohol (ethyl) shows this same tendency. I have wondered whether some of this may not be due to the fact that the tables as used by me were made up from data taken from two different observers. I found two tables for aluminium chloride, both for the

same temperature, but the densities differ from each other by per cents varying up to 2 per cent.

It is impossible in this paper to include the curves for anywhere near all the solutions I have undertaken to study. But I may say I found the curves for sugar, sulphuric acid and zinc sulphate to be perfectly straight, and those for NaOH and nitric acid concave towards the x-axis, thus differing from all the B curves in this report. It is thus clear that we do not as yet possess sufficient data to draw any very general conclusions.

TABLE I.

Class A (Curves Straight or Nearly Straight).

	I.	II.	III.	IV.	V.	VI.
$AgNO_3$	169.94	1.33721×10^{-2}	20	1.15	*c*	.2
Al_2Cl_6	196	.31316	40	1.34	*b*	.5
$Al_2(SO_4)_3$	142.38	.44873	28	1.34	*b*	
$KAl(SO_4)_2$	258.37	.40946	6	1.06		
BaN_2O_6	261.42	.3627	8	1.07	*c*	.03
$BaCl_2$	208.30	.40656	27	1.29	*b*	.6
CaN_2O_6	164.12	.33861	60	1.61	*c*	.5
$CaCl_2$	111.0	.36591	40	1.40	*b*	.2
$Ca(C_2H_3O_2)_2$	158.15	.21807	30	1.59	*c*	.3
$CdSO_4$	208.46	.44936	36	1.47	*b*	.6
$FeCl_3$	162.25	.37271	60	1.67	*c*	.5
$HgCl_2$	270.9	.36208	6	1.05	*b*	.04
$CoCl_2$	129.90	.4287	20	1.23	*s*	.5
$CuSO_4$	159.66	.44767	17	1.2		.17
KBr	119.11	.36241	45	1.46	*b*	.6
KF	58.15	.33216	45	1.43		.04
KCl	74.60	.26996	20	1.34	*b*	.1
KNO_3	101.16	.27688	20	1.14		
K_2CrO_4	194.40	.35784	40	1.40	*b*	.6
LiCl	42.48	.24408	60	1.78	*b*	.3

The column I. gives the molecular weights, II. gives the slope of the line $\log \delta = mc$, III. and IV. give respectively the concentration and density for the highest point (approximately). The last column gives the relative error (maximum) made by taking the density from the logarithmic law rather than from the tables. In the following tables, II. and III., column II. gives the slope of the average straight line. Column VI. is omitted; the per cent. errors range from .8 to about 5.

TABLE II.

Class B (Sloping Uniformly Upward or Downward).

	I.	II.	III.	IV.	V.
$Ba(C_2H_3O_2)_2$	255.45		40	1.36	irreg.
$BaBr_2$	297.32		50	1.69	
BaI_2	391.34		60	1.97	
$CaBr_2$	200.02	$.4062\times10^{-2}$	50	1.64	
CaI_2	294.04		50	1.91	
$CdCl_2$	183.30		60	1.89	
$CdBr_2$	272.32		50	1.68	
CdI_2	366.34		50	1.68	
$CuCl_2$	134.60	$.43767\times10^{-2}$	40	1.53	
CuN_2O_6	187.62	.40938	44	1.54	2 st. lines.
$FeSO_4$	151.96	.41947	44	1.56	
$Fe_2(NO_3)_6$	483.86	.34666	60	1.66	
$Fe_2(SO_4)_3$	400.	.42159	44	1.56	max. error 1.5.
KI	166.12	.36735	60	1.73	
LiI	134.04	.3848	55	1.58	
LiBr	86.99	.33575	40	1.26	

TABLE III.

Class C (with Double Curvature).

	I.	II.	III.	IV.	V.
$CO(N_2O_6)$	56.16	$.39603\times10^{-2}$	40	1.47	*s*
KOH	183.02	.3673	54	1.60	
CdN_2O_6	236.42		50	1.76	irreg.

A survey of the tables shows (1); that the majority of the class *A* (which we may call linear salts) are electrolytes. Also a majority of the non-linear salts are non-electrolytes. From the salts which do not run to concentrations above 20 per cent. we can draw no conclusions, as they are practically linear.

2. If the salts of class *A* are plotted, with molecular weights as abscissæ and slopes of the straight lines as ordinates, we obtain a "target diagram" from which we can draw no conclusion.

3. Among the non-linear salts we find that most of them run up to rather higher concentrations and densities than most of the linear salts. However we should not forget that sugar and sulphuric acid, both of them linear, run up to concentrations of 65 and 100 per cent. respectively.

4. It does not appear that any element is confined to one class or the other; nor does it appear that an acid radical appears in only one class.

5. We may suggest also that organic salts will be found among the linear class, judging from the fact that sugar is linear.

It is evident that the present question is closely connected with that of the freedom of motion of molecules. In gas theory this is the starting point for many a theoretical discussion. But then gas molecules move about with more freedom than do molecules in a

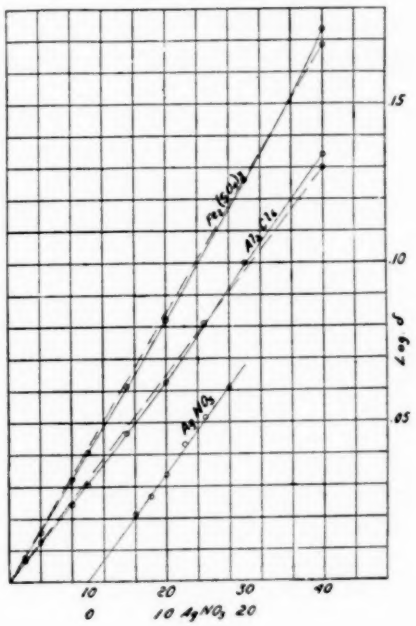

Fig. 12.

solution. However we can imagine that at first molecules enter with ease. But after a while this is not so much the case. Still we cannot make any suppositions as to how the freedom of these molecules depends on the number already present but must derive any equations of that sort from known equations. We can certainly see that as a chemical whose density is greater than that of the solvent is introduced, the density of the solution must be between that of the chemical and that of the solvent, and that as more and

more of the chemical is introduced, the density increases faster. And anything that differs from this points to something strange.

It seems reasonable that the relative increase in the density, produced by the addition of a chemical, should be simply related to the increase in the concentration. Our proposed equation, when differentiated, gives

$$\frac{d\delta}{\delta} = \log_e 10 \cdot m \cdot dc.$$

Is it possible that the question is related to that of dissociation? Perhaps the density of a solution in which all molecules are dissociated is different from that in which none are dissociated. And

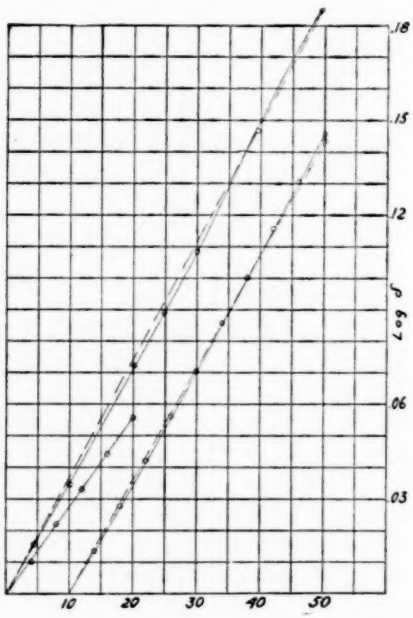

Fig. 13.

if the dissociation depends on the number of molecules already present (*i. e.*, on the concentration) then we can see why the shrinkage is not proportional to either density or concentration. Perhaps it will be possible from the correct equation for any one salt to arrive at an equation which shall say how dissociation depends on the concentration.

One of the things we should be able to calculate from our equation is the density of the salt itself. The law may hold for the solution up to saturation, but if it holds up to a concentration of 100 per cent. it is more serviceable. Now in the case of common salt, the

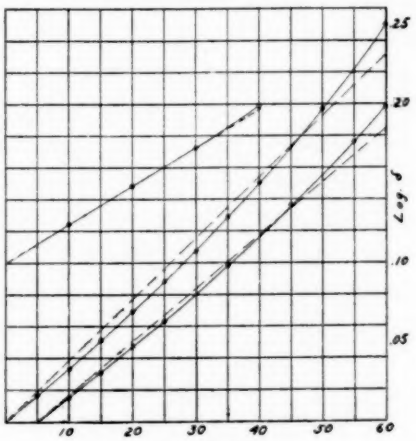

Fig. 14.

density for a concentration of 25 per cent. is 1.1897, and the logarithm of the density is .075438. The logarithm for a concentration of 100 per cent. ($=4\times25$) would be four times as great, hence .301752, whose antilogarithm is a trifle over 2; the density of common salt is about 2.15, not so very different when one considers that the computation was made by an extrapolation for a point whose distance from the last point of the curve is three times the length of the curve.

Another property which our equation should possess is that from it we should be able to determine at what density or concentration the solution is saturated.

The law, as now proposed, seems to need modifications of some sort. Perhaps in its completed form it will be to solutions what Dalton's law is for the physical mixture of gases. There are many things to be said in favor of the present equation, however. Like Boyle's law, it answers only approximately to the actual facts, but it was discovered, like Boyle's law, by the study of a case where it applied certainly to a degree of accuracy as great as the measurements from which it was derived. Its great advantage is simplicity,

and from it we can derive many important facts. Its deviation from the true facts, as in the case of Boyle's law, is not the same for every substance nor for every temperature. On the other hand, the errors of Boyle's law have led to the discovery of the very things that made it possible to improve on it, as well as the discovery of other important things.

Then there are two ways in which a simple equation may serve: If it be true for an ideal case, it will serve as the basis of many a theoretical discussion leading to more or less correct results. If it be not true, it may serve as the starting point for finding a better

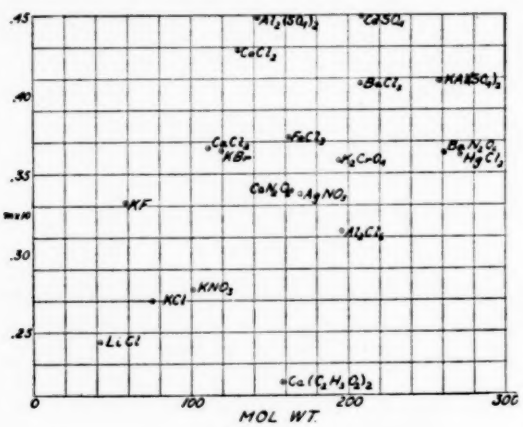

Fig. 15.

equation. It is not claimed that my equation is any better than Boyle's law. It is merely presented as a first step. Then if it is shown to be true, it may perhaps lead to the discovery of phenomena at present unknown.

The curves in Figs. 3–14 are those catalogued in Tables I., II. and III. of this paper. Fig. 15 is the target diagram already referred to.

RÉSUMÉ.

The densities and concentrations of solutions of common salt in water are connected very accurately by the very simple equation $\log = mc$, in which m is a constant. This gave rise to the question whether perhaps this law also applies to the solution of other chemicals. It is with this question that this paper is chiefly concerned.

Of the solutions studied so far, it was found that the solutions whose maximum concentration is less than 15 per cent. obey the law very well; of the others, about one half obey the law within .6 per cent. Of those that are listed in this paper, about half are electrolytes, and the other half are not; and the electrolytes seem to be mostly confined to the linear solutions. The number of salts studied is not great enough to permit any very definite and general conclusions to be drawn.

It is not known now whether the law proposed is only an approximate law, or whether it is a law applying to an ideal condition. In either case it may lead to the discovery of important facts.

It is furthermore suggested that the law may throw light on various other questions: (1) On the problem of the molecular behavior of chemicals, (2) on the problem of osmosis, (3) on the laws governing the mixture of more than two substances.

The law when properly modified may be used to calculate: (1) the density of a solution for any concentration; (2) hence also the density for a concentration of 100 per cent., *i. e.*, the density of the pure chemicals, (3) the concentration of the saturated solution.

That the present law, though as yet imperfect, is rich in possibilities, is at once evident. It is hoped that a further contribution on the subject may be made soon.

DISCHARGE FROM HOT CAO.

BY C. D. CHILD.

IT was suggested a few years ago by Sir J. J. Thomson[1] that certain phenomena of electrical discharge could be explained by what we may call ionization by *repeated* impact. He had found that luminous discharge could be produced from a cathode of hot CaO with potential differences much smaller than those which are needed when a cold cathode is used, and that at a certain critical point it needed but a very small increase in the voltage to produce a large increase in the current and to change from the non-luminous to a luminous form of discharge. He believed that the ionization in the luminous form of discharge was not due to the breaking up of an atom by a single impact with an electron, but rather to an explosion of the atom because of its having absorbed so much internal energy from repeated impacts with electrons that its equilibrium had become unstable.

If this idea is correct, it is important not only because it explains this particular phenomenon, but also because it offers an explanation of the ionization of the arc and gives us some information concerning the character of the atom. I have, therefore, given some study to the subject, but find that there are several reasons for rejecting this explanation.

Improbability of Repeated Impacts.—The first of these objections is that there are far too few electrons present in the tube at any time before the discharge becomes luminous to occasion repeated impacts. For example, in one experiment performed by myself the largest current that could be passed through the tube without having a luminous discharge was 5×10^{-9} ampere, which is 150 electrostatic units. The charge carried by each ion[2] is 3.4×10^{-10}. The cross section of the tube used was approximately 5 sq. cm. So that the number of electrons passing through each square

[1] Nature, 73, 496, 1906.

[2] Thomson's Conduction of Electricity through Gases, 2d ed., p. 158.

centimeter per second was 8.85×10^{10}. The pressure of the gas was .014 mm. and the mean free path of the electron at this pressure is approximately 3.76 cm.[1] So that in each cubic centimeter only 2.34×10^{10} electrons would hit molecules per sec.

According to Myers[2] there will be 11.2×10^{14} molecules per c.c. under these condition of pressure and temperature. From this we find that each molecule will on the average be hit once in 48,000 sec., or once in thirteen hours, and it only requires a fraction of a second to produce the luminous discharge when the conditions are right for it.

This is, of course, not an argument against ionization by repeated impact after the luminous discharge has commenced, for then the number of electrons will be very much greater, but the idea of such impact was used by Thomson as an explanation of the beginning of the luminous discharge, and it is an argument against such an explanation. There will, however, be other data given later which indicate that not at any time is there ionization by repeated impact.

Critical Condition Does not Depend on the Amount of Current, but on the Condition of the Cathode.—In the second place experiments indicate that the voltage required to change from the non-luminous to the luminous discharge depends but slightly, if at all, on the amount of current flowing, but does depend very greatly on the kind and condition of the cathode. That is, the number of electrons passing through the tube and hitting upon the molecules does not determine the point where the change occurs, while other conditions do.

The form of apparatus used for showing this is given in Fig. 1. *T* is a tube 2.8 cm. in diameter. *P* is the connection to the vacuum pump, McLeod gauge, and drying tube. *C* is the cathode consisting of platinum foil, approximately 2 mm. in width, 12 mm. long, and .02 mm. thick, the bottom being covered with CaO. This was welded to aluminum wires which led out of the tube and was heated by an alternating current connected at *c* and *c'*.

A is an iron anode, fastened to an iron wire which is brought down through the tube *a* into a mercury cup, so that the anode

[1] Idem, p. 476.

[2] Myers' Kinetic Theory of Gases, p. 333.

could be raised or lowered. A shunt of 50 ohms resistance was placed across cc'. The middle of this, lettered b, had the same potential as the middle of the foil C. A potential difference was maintained between b and A by connecting them to d and d', two points on a variable resistance through which a current was passed from a dynamo. By this means any potential difference from 0 to 130 could be used. V is a Weston voltmeter measuring this potential difference. G is a galvanometer measuring the current through the tube.

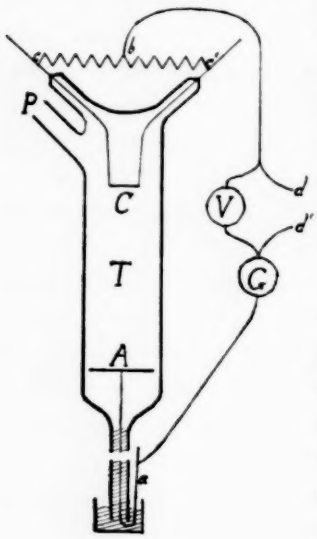

Fig. 1.

The first experiment was a comparison of the discharge from clean hot platinum with that from hot platinum covered with CaO. With clean platinum it is possible to get a large current without changing the character of the discharge, while with CaO it requires but a very small current to produce this change, the potential difference between the electrodes being the same in the two cases.

In order to get as large a current from the platinum as possible it is desirable to perform the experiment before the occluded gas has been entirely driven off. If this is done, the current is continually changing, so that no two sets of readings are the same, but this does not interfere with our present purpose.

The readings as taken are given in Table I., the first column giving the potential difference between the electrodes and the second the current. The platinum foil was a little more than red hot and the pressure of the gas was approximately .04 mm.

TABLE I.

Potential Difference in Volts.	Current in Amperes Times 10^{-7}.
71	.1
80	.5
84	2.1
90	6.5
125	48.2

There was here no abrupt change in the amount of current and the discharge was not at any time luminous. There is in some cases a slight luminosity with the discharge from clean platinum, but even then there appears to be no sudden increase in current nor sudden change from non-luminous to luminous discharge.

On the other hand with hot CaO the discharge changes to the luminous form before anything like this amount of current passes through the tube. This is especially true when the cathode is quite hot and has been used until the occluded gases have been driven off. In one case it was impossible to pass more than 5×10^{-9} ampere with a potential difference of 95 volts without the discharge becoming luminous. When the voltage was raised above this, the current became as large as an ampere or more, if the resistance in series with the tube was small.

Thus we see that the discharge remained non-luminous quite irrespective of the amount of current passing, provided the cathode was clean platinum and that it very quickly changed to the luminous form, if the cathode was very hot CaO.

Thomson states that he found the voltage at which the change took place to depend on the current, but in his experiments the current was changed by raising the temperature of the cathode. When that is done, it is not possible to decide whether the critical point depends on the current or on the temperature of the CaO. In the experiments described above it is made clear that it is the condition and temperature of the cathode that determines this point and not the amount of current.

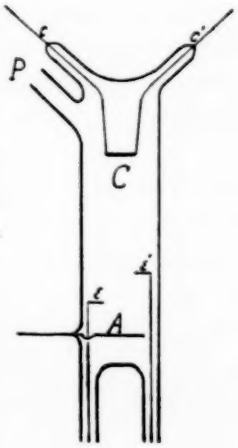

Fig. 2.

The Potential Difference between the Beginning and End of a Striation.—The potential difference between the beginning and end of a striation was examined, hoping that it would throw some light on this question.

The tube was exchanged to the form shown in Fig. 2. Both A and C are here fixed; e and e' are two movable exploring electrodes which are connected to an electrometer. The

vertical parts of these were covered with small glass tubes for a few centimeters near the top, so that only the horizontal ends would receive charges. These ends were platinum wires .5 mm. in diameter. They were placed as near as possible to the sides of the tube and did not appear to distort the striations. The main tube was 4.2 cm. in diameter. The distance between A and C was 8 cm. The length of a striation varied as the pressure of the gas was varied, but was in general in the neighborhood of 2.5 cm.

It was first of all observed that the potential difference which was being studied varied as the pressure of the gas was changed. This is shown in Table II. The first column gives the pressure of the air left in the tube, and the second the potential difference between the beginning of one striation and that of the next. The current was .02 ampere.

TABLE II.

Pressure of Gas in Millimeters.	Potential Difference in Volts.
.06	11
.08	12.9
.164	16
.38	23.5

It was also found that the striation potential difference depended on the amount of current flowing through the tube. This is shown in Table III., where the first column gives the current and the second the potential difference. The pressure in the gas was .06 mm. of mercury.

TABLE III.

Current in Amperes.	Potential Difference in Volts.
.00032	14
.00064	13.2
.01	12
.2	10

Since these experiments were performed an article has been published by Wehner,[1] giving the results of a full investigation of the striation potential difference when there was discharge from a cold cathode. His experiments on the change produced in this quantity when the pressure of the gas was changed were performed in hydrogen and the potential differences which he gives are lower than the ones given above, but they show the same kind of a change.

[1] Ann. d. Phys., 32, 49, 1910.

In general he also found the same kind of a change when the current was changed. The changes, however, were through a much smaller range than that given here and were accordingly less noticeable. The lowest value which he found for the potential difference was 8.56 volts.

At first sight Table III. appears to give some reason for believing that ionization may take place more easily where there is a chance for repeated impact. Certainly it is true that where there is the greatest number of electrons passing through a gas, there is the smallest striation potential difference, and it is probable that this quantity is closely related to the potential difference needed to produce ionization by impact, as is suggested by Wehner.

But a second thought will hardly encourage such a view. The current was six hundred times greater in the last case given in the table than in the first. Each molecule would be hit six hundred times in one case where it would be hit but once in the other, and yet the potential difference decreased but a few per cent. It is certainly highly improbable that such a small change would occur, if repeated impact causes the molecules to be more easily ionized.

Certainly it is possible to suggest some more probable explanation. For example, when the larger current is flowing, the temperature of the gas must be much above that of the room. A small percentage of the electrical energy dissipated in the tube would be sufficient to raise the temperature of the gas several hundred degrees in a few seconds and it is altogether probable that at high temperatures the gas is more easily ionized than at low ones.

However, we will not be ready to give any explanation of these facts until we know more about what the facts are. For example, the lowest voltage here recorded was 10 volts, but Thomson states[1] that he found the potential difference between one striation and the next to be as low as 2.7 volts under certain conditions. He does not state what these conditions are, and I have not been able to get such a value. But until the phenomena have been more thoroughly examined, it is not possible to state what the cause of the relation between the voltage and the current is, and certainly we cannot say that these phenomena uphold in any way the idea that ionization occurs more easily when there is repeated impact.

[1] Phil. Mag., 6, 18, 449, 1909.

Increase in Current not due Alone to Ionization in the Gas.—We have given reasons for believing that the change from the non-luminous to the luminous form of discharge is not due to ionization by repeated impact. We may go a step further and say that the change does not appear to be due alone to ionization of any kind in the gas. There is no question but that ionization by impact occurs, but there are reasons for believing that it is not the only cause producing the change.

There are two ways in which ionization in the gas can increase the current. It can increase the number of positive ions moving toward the cathode, or it can change the field near the cathode, so that all the electrons shall be drawn from it, instead of being driven back by the electrostatic repulsion of those which had previously been emitted.

That the great increase in the current cannot be accounted for by a movement of positive ions toward the cathode is shown by two lines of reasoning. The first is that the electrostatic effect on the positive ions would check any large increase in the current due to them alone.

The Electrostatic Effect Produced by Ions.—An electrostatic effect occurs whenever there are more ions of one kind than of the other in a given volume. This effect may become so large as to reverse the previous direction of the field and to limit very greatly the amount of current flowing. This is especially apt to occur when there are positive ions present, for their mass is much greater than that of the negative ions and their motion correspondingly slower.

The ratio of the mass of positive ions to their charge is approximately 20,000 times as great as the corresponding ratio for the negative ions.[1] As a result one positive ion going through a given space per second would neutralize the effect of 20,000 electrons. If there were more positive ions than this they would raise the potential of the region and tend to check their own movement.

It is not possible to compute just how many positive ions it would take to raise the potential so as to check the current when the cathode is an irregular piece of foil, but we may get some idea of what is to be expected by considering the current density between

[1] Thomson's Conduction of Electricity through Gases, 2d ed., p. 149.

parallel plates of infinite extent, when there are only positive ions present. The less the ions are stopped by collisions with molecules, the greater will be their velocity and the less the electrostatic effect produced by the movement through the field of a given number. In order to find the maximum current, we may assume that there are no collisions. I have not been able to find any computation applying to this case, and hence have given it in the following paragraphs.

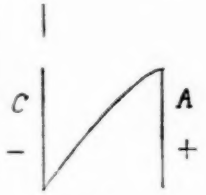

Fig. 3.

Let us assume that the plates A and C are of infinite extent, separated by a distance x_1. Let the potential of C be zero and that of A be V_1, and assume that there are at A an indefinitely large number of positive ions. The electric force will cause these to move toward C, producing a current.

Let I = the current flowing through a unit cross section,
n = the number of ions in a unit volume,
ϵ = the charge in electrostatic units carried by each ion,
m = the mass of each ion,
V = the potential in electrostatic units at any point at a distance x from C,
v = the velocity of the ions at a distance x from C,
ρ = the density of the electricity at a distance x from C.

$I = n\epsilon v$ = a constant, and the acceleration of the ions equals the charge times the electric force divided by the mass, or

$$\frac{dv}{dt} = -\frac{\epsilon}{m}\frac{dV}{dx}.$$

If we multiply this equation by the equation, $vdt = dx$, and integrate, remembering that the velocity is zero when V is V_1, we have

$$\frac{1}{2}v^2 = \frac{\epsilon}{m}(V_1 - V) \qquad \text{or} \qquad v = \left\{\frac{2\epsilon}{m}(V_1 - V)\right\}^{\frac{1}{2}}.$$

But

$$\rho = n\epsilon = \frac{I}{v} = \frac{I}{\left\{\frac{2\epsilon}{m}(V_1 - V)\right\}^{\frac{1}{2}}}$$

and if we assume that there is no variation in potential in directions

parallel to the plate we have

$$\frac{d^2V}{dx^2} = -4\pi\rho = -\frac{4\pi I}{\left\{\frac{2\epsilon}{m}(V_1 - V)\right\}^{\frac{1}{2}}} = -\frac{k}{(V_1 - V)^{\frac{1}{2}}}$$

where k is a constant equal to $4\pi I/\sqrt{2\epsilon/m}$.

Multiplying this by the equation

$$\frac{dV}{dx}\,dx = dV$$

and integrating, we have

$$\frac{1}{2}\left(\frac{dV}{dx}\right)^2 = 2k\,(V_1 - V)^{\frac{1}{2}} + C.$$

The constant, C, equals the value of $\frac{1}{2}(dV/dx)^2$ at A. As the space between A and C becomes more and more filled with positive ions, the value of dV/dx approaches zero, and for the largest current which it is possible to have it would equal zero. For such a current we have

$$\frac{dV}{dx} = 2\sqrt{k}(V_1 - V)^{\frac{1}{2}}.$$

Further integration gives us

$$V = V_1 - (V_1^{\frac{3}{2}} - \tfrac{3}{2}\sqrt{k}\,x)^{\frac{2}{3}},$$

since $V = 0$ when $x = 0$. The curve in Fig. 3 between A and C represents such a distribution of potential as this.

Since V_1 is the value of V when $x = x_1$, we have

$$\tfrac{3}{2}\sqrt{k}\,x_1 = V_1^{\frac{3}{2}}$$

or

$$I = \frac{1}{9\pi}\sqrt{\frac{2\epsilon}{m}}\,\frac{V_1^{\frac{3}{2}}}{x_1^2}.$$

In other words, this is the largest current which it is possible to have carried by positive ions with the given distance and the given potential difference between the plates.

The value of ϵ/m for positive ions in electrostatic units is approximately 12×10^{12}.[1] If for example we take one third of an electro-

[1] Thomson's Conduction of Electricity through Gases, p. 149.

static unit (100 volts) for the potential difference between A and C and the distance 4 cm., the current would be 2.08×10^3 electrostatic units, or 7×10^{-7} ampere. This is the amount of current which could be carried if there were only positive ions, or the amount carried by the excess of positive ions. A certain amount might be carried by negative ions, a second small amount by the positive ions which would be needed to neutralize the electrostatic effect of these negative ions and the amount given above would be the greatest possible additional amount which the excess of positive ions could carry.

The potential difference and distance assumed are similar to those existing in the experiments which have been described. The shapes of the electrodes in the experiment were indeed quite different from those considered in the mathematical treatment. But when we remember that it was possible to have an increase of nearly an ampere per sq.cm. a few centimeters away from the cathode and of many times this density of current near the cathode, we can see how improbable it is that any such increase in the current was carried by positive ions coming from the gas.

But an even more convincing reason for believing that the increase in current is not produced by a movement of the positive ions toward the cathode is given by the appearance of the luminous discharge. With non-luminous discharge there were, of course, no streams of cathode rays which could be detected. With the luminous discharge there were very noticeable cathode rays, appearing as brilliant streamers extending from the cathode to the sides of the tube or down into the gas. That these were cathode rays was shown by the effect which a magnet had upon them and by the phosphorescence which they produced. One could hardly see these streamers without realizing that something had happened to increase enormously the number of electrons leaving the cathode.

Increase in Current not due to Change in Field.—While the increase in current cannot be due to the movement of positive ions, it is conceivable that it is due to a change in field produced by them. When there is no ionization of the gas, the electrons coming from the cathode may be so numerous as to reverse the direction of the field in part of the space and hold back other electrons which may

be leaving the CaO. That this actually could occur is shown by the data given in Table IV. When there are also positive ions in the field, they may so neutralize the effect of the electrons, that all the electrons which escape from within the CaO will pass to the anode. In order to consider this possibility the potential between the electrodes was examined both with non-luminous and with luminous discharge.

Potential between the Electrodes.—The apparatus shown in Fig. 2 was used to measure the potential between the electrodes, and since only one exploring wire was needed, e' was removed.

There are given in Table IV. a series of readings of the potential between A and C taken when the cathode was a dull red and a non-luminous current of 1×10^{-8} ampere was passing through the tube. In Table V. there is given a similar set taken with a luminous current of .03 ampere. In both cases the pressure of the gas was .02 mm. This was so low that there were no striations nor anode glow between the electrodes. The potential difference between A and C was 90 volts, and the distance 8 cm. Column one gives the distance from C and column two the potential difference between C and the exploring electrode as measured by an electrometer.

TABLE IV.

Distance from Cathode in cm.	Pd between C and e in Volts.
.3	−1.
2.	0.
4.	3.2
6.	7.7
7.	14.3

TABLE V.

Distance from Cathode in cm.	Pd between C and e in Volts.
.3	71
2.	71
4.	69
6.	69
7.	66

The first value in Table IV. indicates that the potential of the gas near the cathode was slightly lower than that of the cathode itself. This is due to the tendency of the CaO to give out electrons faster than the field draws them away, in fact to emit them against a small electric field, as has been pointed out by Richardson.[1]

[1] Phil. Mag., 6, 16, 354, 1908.

In the second case the same kind of an effect occurs except that here the electric force is reversed not near the cathode but a few centimeters from it. This fact has been observed by Thomson.[1] The momentum of the ions is such that it carries them for some distance against the opposing field.

The potentials here given are much lower than those given by Westphal.[2] He was undoubtedly working with much higher temperatures than those existing in these experiments.

There results are plotted in Fig. 4, the first curve showing the

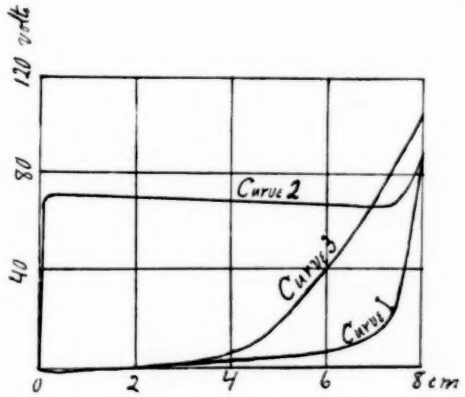

Fig. 4.

potential when the discharge was non-luminous and the second when it was luminous. With the first one there is an excess of negative ions between the electrodes, with the second an excess of positive. In the first case there is little or no ionization in the gas, while in the second there is a large amount. This might at first lead one to think that the difference between these two forms of discharge was entirely due to the presence of the positive ions near the cathode and the resulting drop in potential at that point. For this would cause all of the electrons which might escape from within the CaO to pass through the tube, but further light is thrown on the matter by examining the potential between the electrodes when discharge is passing from clean platinum.

For this purpose clean platinum was substituted for that covered

[1] Phil. Mag., 6, 18, 442, 1909.

[2] Deutsch. Phys. Gesell. Vehr., 10, 11, 401, 1908, and Science Abs., 11, p. 519.

with CaO and observations were taken with the platinum heated to a bright red. The potential difference between the electrodes was 90 volts and the current through the tube was 5×10^{-7} ampere. The potential at different points was found to be approximately the same as those given in Table IV., when there was non-luminous discharge from CaO.

TABLE VI.

Distance from Cathode in cm.	Pd between C and e in Volts.
.3	−1.
2	− .4
4	4.5
6	42.
7	70.

These data are plotted in curve three, Fig. 4. There is here little change between this curve and that found with small currents as far as the space near the cathode is concerned, but a large change near the anode. There is apparently ionization of the gas near the anode, but not enough positive ions are produced to change the potential of all the space.

By raising the temperature of the platinum still higher a current of 4.8×10^{-5} ampere was passed through the tube. The potential in the neighborhood of the cathode was unchanged, while that in the neighborhood of the anode was still further raised. For example, the potential 6 cm. from the cathode became 68 instead of 42 volts.

Fig. 5.

It is apparent that this form of discharge is not the same as either the non-luminous or the luminous form of discharge from CaO, since we have some ionization of the gas and yet there is no great change near the cathode. Apparently something besides ionization in the gas is needed in order to produce this change. *Some Ionization of the Gas Necessary.*—While something besides ionization of the gas appears to be necessary in order to change from the non-luminous to the luminous discharge, it is also necessary that there should be this ionization, as is shown by the following experiment.

Two pieces of platinum wire, C and C' in Fig. 5, are surrounded by brass cylinders of different diameters and placed in a vacuum

tube. Both wires were .5 mm. in diameter, had the same length and were heated by the same current. They were coated with CaO and were made the cathode with the cylinders as anodes. The smaller cylinder was 4.85 mm. and the larger 23 mm. in diameter. Both were 4.5 cm. in length. The potential difference between the wires and the cylinders was in all cases 90 volts. There are given in the following table the currents to the cylinders with two different pressures of the gas.

TABLE VII.

Pressure of Gas in mm.	Current to Small Cylinder in Amperes.	Current to Small Cylinder in Amperes.
.35	.01	8×10^{-3}
.014	5.8×10^{-6}	1.6×10^{-3}

This shows that the current to the small cylinder decreased very much when the pressure of the gas was diminished below a certain amount, and that at the same time the current to the large cylinder increased. The number of electrons coming from within the CaO was no doubt the same for both wires, and the electric force was, of course, in both cases larger for the small cylinder. In the first case the discharge to the small cylinder was the larger, as one would expect, since the electric force was larger. Apparently the small discharge to the small cylinder in the second case is due to the fact that there were then so few molecules within the cylinder that there was less opportunity for impact and consequently there was little ionization. It would, therefore, appear that while ionization of the gas is not the only requirement, it is at least a necessary requirement.

The Correct Explanation.—It has already been stated that much smaller potential differences are adequate to produce luminous discharge from hot CaO than from any cold cathode, but this is practically the only difference between the two cases. In both the luminous discharge commences with great suddenness and in both there are streams of electrons shooting out from the cathode. It would, therefore, seem as if some modification of the explanation which Thomson has given for the ordinary discharge in a vacuum would come nearer the truth than that which was suggested.

His explanation for such discharge is briefly as follows: The current through the tube is carried by ions. The production of these is a two-fold action. Negative ions which have been driven off from the cathode hit the molecules of the gas and ionize them by their impact. The positive ions thus formed are drawn up to the cathode and ionize the molecules at the surface of the cathode by their impact on them. The negative ions thus formed repeat the process by ionizing more molecules of the gas. The electric force in the tube must be sufficient to produce ionization at both of these places, but since it requires a much higher potential difference to ionize by the impact of the positive ions, it comes about that the critical potential difference is reached when such ionization begins.

It is altogether probable that the same thing occurs in the case of discharge from hot CaO, the only difference being that the molecules on the surface of the hot CaO are more easily ionized than those on the cold cathode, and there are reasons for believing that this is true, as will be given shortly.

If we make this assumption the phenomena may be explained as follows: As soon as the electric force is great enough to ionize the gas, we have a slight increase in current, such as is shown with the discharge from clean platinum. This increase does not become large, unless the positive ions thus formed are able in turn to produce ions by impact on the surface of the CaO. When this occurs, the greater the number of positive ions formed in the gas, the greater the number bombarding the cathode with the corresponding further increase in the number of electrons sent off. There is thus produced the sudden change in current which occurs at the critical point. This change is limited by the rise in potential between the electrodes which is caused by the presence of the positive ions. When this increase becomes so large that the ions are not carried to the electrode as fast as formed, the current remains stationary.

This sudden increase is probably helped by the fact that the rise in potential in the tube causes the principal drop in potential to be near the cathode, instead of near the anode. The electrons coming from the cathode have a certain velocity when first emitted. A drop in potential in its immediate neighborhood increases this and produces a greater final velocity than if applied to electrons which might be starting from rest at some point in the gas.

There are the following reasons for believing that the molecules on the surface of the cathode are more easily ionized by impact of positive ions when the cathode is hot than when cold. Due to their high temperature they are already in unstable equilibrium, as is shown by their sending out electrons even when not being bombarded. One would in fact be surprised, if it did not require a smaller momentum in this case to produce ionization than when the molecules are at a low temperature.

Secondly it has been shown by Hittorf[1] and Cunningham[2] that heating the cathode causes the cathode drop to become smaller.

Furthermore I have found that the higher the temperature of the CaO the less the cathode drop in its neighborhood. The drop given in Table V. was 71 volts, but when the temperature of the CaO was raised, this decreased rapidly. When heated as much as practical without melting the platinum foil, the cathode drop was only 8 volts.

Increasing the current through the tube also decreased the cathode drop but only to a slight extent. Thus in one case the current was varied from .02 to .4 ampere by changing the voltage at the terminals of the tube, the heating current through the foil remaining constant, and the cathode drop varied from 30 to 21 volts. The same change could be made by a very slight increase in the current heating the foil, and it is altogether probable that this change was due to the increase in the temperature at the surface of the cathode caused by the increased bombardment of the cathode and not by repeated impact on the molecules of the CaO.

Production of Electrons by Bombardment of CaO with "Canal-strahlen."—In addition to this it was shown that electrons may very easily be produced when CaO is bombarded with positive ions in the form of "canal-strahlen." It has already been shown by Austin[3] that when such rays strike a metal plate electrons are produced, but it seemed well to investigate the phenomena which exist when they strike hot CaO under conditions somewhat similar to those which held in the preceding experiments.

[1] Wied. Ann., 21, 133, 1884.
[2] Phil. Mag., 6, 4, 684, 1902.
[3] PHYS. REV., 22, 312, 1906.

For this purpose the tube given in Fig. 6 was used. An opening was made in the side of the tube shown in Fig. 1, and a second tube, T', was sealed into this. This had a cathode, C', and an anode, A', the distance between them being 9 cm. The anode, A', was a metal disk filling the inside of the small tube and having an opening of 2 mm. in diameter in the center. A discharge could be sent through this tube by means of a Wimhurst machine or an induction coil at I and with proper pressure of the gas "canal- strahlen" would hit on the cathode, C. The anode A' was kept at the same potential as C by connecting it to the point b shown in Fig. 1.

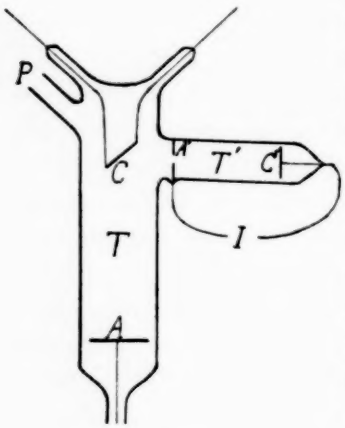

Fig. 6.

With this arrangement C was heated by passing a current through it as in the preceding experiments and a potential difference was established between A and C somewhat below that needed to cause the luminous discharge. If then a discharge was caused to pass from A' to C' so that the "canal-strahlen" hit upon C, luminous discharge would start up in T. With potential differences of about 70 volts this discharge would pass as long as C was being hit by these rays and would stop as soon as the rays would stop.

With larger voltages a continuous arc was often formed. With lower voltages the discharge between A and C was non-luminous but still considerably larger than what it was when there were no "canalstrahlen."

It was found that it was not even necessary to heat C. When C was at the room temperature, and the voltage was approximately 100 volts, the positive rays striking on C caused a luminous discharge between A and C to flash out for an instant. This luminous discharge showed striations the same as those usually produced by hot lime, and if the resistance in series with A was sufficiently small, the discharge became an arc.

Relation between this Work and the Theory of the Electric Arc.—

The work which has been described has an important bearing on the theory of the electric arc. There is no question but that the ionization at the cathode is the essential phenomenon of the arc, but there are two views concerning the cause of this ionization. According to Stark[1] and Thomson[2] the electrons are driven out of the cathode because of its high temperature in the same way as discharge is produced from hot platinum wire. The bombardment of the cathode by the positive ions heats it, but does not directly cause the ionization.

According to the other view the ionization at the cathode is produced directly by the bombardment of the positive ions on the molecules on the surface of the cathode, the same as in the Geissler tube discharge, the cathode drop in the arc being smaller than elsewhere, because a smaller potential difference is needed to produce ionization when the molecules of cathode are hot.

There are some rather serious objections to the first view. For example, mercury can be the cathode of an arc in a vacuum, although it cannot be raised to anything like a high temperature in a vacuum without changing it to a vapor. On the other hand, iron can easily be heated to a point where it will give off electrons, and yet it cannot be made the cathode of an arc in a vacuum.[3]

In addition to these arguments the work which is here described furnishes a further argument in favor of the second view. The arc is apparently the same form of discharge as that which we have been studying, for it has been shown[4] that it is possible to pass by gradual changes from the luminous discharge produced by hot CaO to that of the electric arc. The only essential difference between the two is that in the arc the current through the gas heats the cathode sufficiently to maintain the temperature of the cathode, while in the other form the temperature must be maintained by some outside source, and this difference has nothing to do with the manner in which the ions are produced.

We are, therefore, safe in saying that the weight of evidence is in favor of the view that the ionization at the cathode of the arc

[1] Ann. d. Phys., 12, 673, 1903.

[2] Conduction of Electricity through Gases, 2d ed., p. 612.

[3] PHYS. REV., 20, 369, 1905.

[4] PHYS. REV., 29, 361, 1909.

is not caused by the high temperature of the cathode, but by the impact of positive ions on the hot surface.

Summary.—When the potential difference between the electrodes is increased the discharge in a vacuum from hot CaO passes through a critical condition, the current being very much greater after the critical point is passed and the discharge becoming luminous. It has been suggested by Sir. J. J. Thomson that this sudden change is caused by the molecules having been hit so often by the electrons that many of them are in a state of unstable equilibrium, and that when in this state but a small increase in the electric force is needed to cause ionization.

There are the following reasons for thinking that this is not the correct explanation. First, the scarcity of electrons present in the tube render such repeated collisions very improbable. Secondly, the potential difference necessary to cause this sudden change does not depend on the number of electrons passing through the tube but does depend on the condition and temperature of the cathode. Third, an examination of the potential gradient through the tube leads us to believe that the sudden increase in current is caused by something other than an increase in the ionization in the gas. Lastly the appearance of the discharge indicates very plainly that the number of electrons streaming from the cathode increases enormously when the discharge becomes luminous, becoming in fact very noticeable streams of cathode rays. On the other hand, some ionization of the gas appears to be necessary as is shown by the fact that, when the pressure of the gas is very low, the discharge from a wire coated with CaO to a small surrounding cylinder is much smaller than that to a large cylinder.

The phenomena may be explained by asssuming that ionizaton is produced at the cathode by the bombardment of its surface by positive ions and that such ionization occurs very much more easily with a very hot cathode than with one which is cold.

The potential difference between the beginning and end of a striation was found to increase as the pressure of the gas increased and to decrease slightly when the current was increased. It was in certain cases as low as 10 volts.

Because of the similarity between this form of discharge and

the electric arc, it is reasonable to assume that the electrons at the cathode of the arc are also produced by bombardment of the cathode by the positive ions which come from the gas, and that they are not to any great extent emitted from within the cathode because of its high temperature. Such an explanation accounts for certain difficulties which may be raised against any other explanation.

COLGATE UNIVERSITY,
January, 1911.

ON POSITIVE ATOMIC CHARGES.

BY FERNANDO SANFORD.

SINCE Faraday's discovery that the same definite quantity of electricity was apparently set free by the electrolytic separation of the combining weight of any univalent element from any compound, it has been believed that univalent ions all carry the same definite charge of negative or positive electricity, and that ions of higher valency carry some simple multiple of this unit charge. Since the discovery and isolation of the unit negative charge great efforts have been made to isolate the corresponding positive charge, but so far without results. This is not surprising, since our present understanding of the phenomena of electrolysis makes the assumption of the unit positive charge unnecessary, as we know of no case where an ion gives off a positive charge to or receives a positive charge from either electrode.

So far as our knowledge extends at the present time, an atom consists of a positive part (subatom) combined with some unknown number of electrons. The positive subatom is generally regarded as the strictly material part of the atom, since the atomic mass seems to be associated with it. A gas molecule, when not monatomic, apparently consists of two or more positive subatoms held together by their mutual attraction for the same electron or group of electrons. These positive subatoms accordingly seem to have permanent electrical charges, and the difference in the force with which they cling to electrons indicates that these charges are different for different atoms.

Many attempts have been made to measure the specific charges of the positive subatoms, but apparently the assumption has always been made that the characteristic charges were simple multiples of charges equal and opposite to the electronic charge, and the results reached have accordingly been difficult of interpretation. The determination of the charge of the alpha particle by Rutherford

and Geiger and by Regener have strengthened the notion of the unit positive charge, since the alpha particles were found to be electrically equal and opposite to two electrons. Accordingly, when the alpha particle combines with two electrons and becomes a helium atom it gives an electrically neutral atom, one which has virtually no affinity or cohesion for other atoms. This is not true to the same extent of any other known atom, and it would accordingly seem that no other atom is so nearly electrically neutral as the helium atom.

There are several methods of separating an atom or molecule into its ions and of estimating the relative charges of these ions. Probably the best known of these methods has been by dissociation in water. In the case of the positive ions in electrolysis we know only the number of electrons which they may take up from the cathode and their average velocity of drift through the liquid under the impulse of a known electric field. We do not know the resistance with which they meet in their movement through the solution, nor through what distances they travel between successive dissociations and recombinations. We know only that if the ions of a given group all have equal positive charges they are acted upon by the same force. If the speeds measured are assumed to be the maximum speeds which the ions can reach in the solution, then the slower ions are slower because they are retarded more than the faster ones, and it is natural to expect the smaller ions to have the higher speeds. The attempts which have been made to apply Stokes's equation to their movement would make their velocities vary inversely as their diameters while, on the contrary, the larger ions of each group have the higher speeds. If we assume, on the other hand, that they move only very small distances as free ions, they will move with accelerated velocities, and if their charges are equal the lighter ions will have the higher speeds. This is again contrary to experience, since the heaviest ions of each group have the highest speeds.

On the other hand, if it be admitted that different subatoms have different electrical charges it is very easy to account for their differences in ionic velocity. While we cannot with certainty calculate the magnitude of these hypothetical charges without knowing more

about the phenomena of electrolysis, we may be justified in making the attempt to see where it will lead.

If the ions in the solution move only from molecule to molecule as free ions their motion will be accelerated according to the equation $F = ma$. Since the force acting on an ion is proportional to its charge, if the ion met with no frictional retardation its charge would be proportional to the product of its mass into its ionic acceleration, and the charges of different ions would be relatively proportional to the products of their ionic masses into their ionic speeds. The following table[1] gives for three well-known groups of elements the ionic charges calculated in this way, the ionic speeds being taken from Lehfeldt's tables. In the last column are given the ratios of the hypothetical charges of corresponding elements in different groups. It will be seen that for each pair of groups these ratios are constant within the limits of our knowledge of ionic velocities, and that within each group the elements are arranged according to their order in the voltaic series.

Element.	Atomic Weight.	Ionic Velocity.	Ionic Charge.	Ratio of Charges.
Cs	133	78.8	10,480	Cs/I = 1.07
Rb	85.5	78.6	6,720	Rb/Br = 1.07
K	39	75.5	2,945	K/Cl = 1.09
Na	23	52.6	1,210	Na/F = 1.17
Li	7	42.6	298	
H	1	365	365	
I	127	77	9,779	I/Ba = 1.04
Br	80	78.1	6,248	Br/Sr = 1.06
Cl	35.5	75.1	2,666	Cl/Ca = 1.07
F	19	54.4	1,034	F/Mg = 1.02
Ba	137.4	68	9,343	Cs/Ba = 1.12
Sr	87.6	67	5,869	Rb/Sr = 1.14
Ca	40.1	66	2,646	K/Ca = 1.11
Mg	24.3	46	1,108	Na/Mg = 1.18

At the time when this table was prepared it was regarded as having significance only in that it served to strengthen a belief

[1] This table was prepared for a paper read before the San Francisco meeting of the American Chemical Society, July 16, 1910, and was published in an abstract in Science of October 7, 1910.

already formed on other grounds that the electrical charge of an atom is as characteristic a physical constant as its atomic weight. Later developments have served to give the figures presented in the table a much higher significance. In a paper by Richardson and Hulbirt in the Phil. Mag., XX., 545, October, 1910, is given a list of values of e/m for a number of positive ions given off by hot metals. The authors express surprise that the values should vary so little for the different metals and attempt to account for this fact by assuming that the ions are not the true subatoms of the metal under investigation, but are due to alkaline impurities in the metals, apparently overlooking the fact that in a previous experiment they found that the ions from the alkali metals were given off with much greater speeds. If the ions are the subatoms of the metals which were heated, the data given by Richardson and Hulbirt enable us to calculate their characteristic charges.

Ten metals were investigated, but of these four gave unsatisfactory results while another, gold, gave two values of e/m. Thus iron gave two values for different samples, and the individual values for the same sample differed by more than 100 per cent. Only one measurement was made on osmium, the single values for tantalum ranged from 115 to 253 and for tungsten from 47 to 541. It seems extremely probable that these metals contained traces of some metals whose ions were more easily given off.

The other six metals belong in two well-marked groups. Their values of e/m and values of e obtained from them by multiplying by the atomic weight are given below. The values of e/m used are those which were determined before they were multiplied by a constant to correct for the error made in determining the value of e/m for an electron by the same method, but as only relative values are considered here this correction is unnecessary.

Element.	e/m	e	Element.	e/m	e
Pt	243	474	Au	139	376
Pd	212	225		280	552
Ni	239	130	Ag	215	232
			Cu	230	146

It will be seen at once that there is a striking similarity between

the relations of the atomic charges calculated in this way and the relation shown in the table calculated from the ionic velocities in electrolysis. It will also be seen that by multiplying the electrolytic charges given by three they become strictly comparable, group by group, with the charges calculated from Richardson and Hulbirt's data. Further, it was seen that in each group the atomic charge varies approximately as the square root of the atomic weight.

In the table below the elements whose charges have been calculated by both methods are given in groups according to their arrangement in the periodic tables. Below each element are given the square root of its atomic weight and its relative atomic charge as calculated above.

H	Li			
1.	2.5			
11.	9.			
F	Na	Mg		
4.4	4.8	4.9		
31.	36.	30.		
Cl	K	Ca		
6.	6.2	6.3		
80.	88.	79.	Ni	Cu
			7.6	8.−
Br	Rb	Sr	130.	146.
9	9.25	9.4		
188.	202.	176.	Pd	Ag
			10.3	10.4
I	Cs	Ba	225.	232.
11.3	11.5	11.7		
293.	314.	280.	?	?
			Pt	Au
			14.−	14.+
			474.	546. and 273.

The relation is still better shown in the accompanying curve where the atomic charges are used as abscissas and the square roots of the atomic weights as ordinates. It will be seen that with the exceptions of lithium and hydrogen the charges are very approximately proportional to the square roots of the atomic weights, and that the charges calculated from the two entirely different

sets of data fit the curve equally well. Strictly speaking, the elements of each group seem to lie on a curve of their own, but these curves are parallel and very close together.

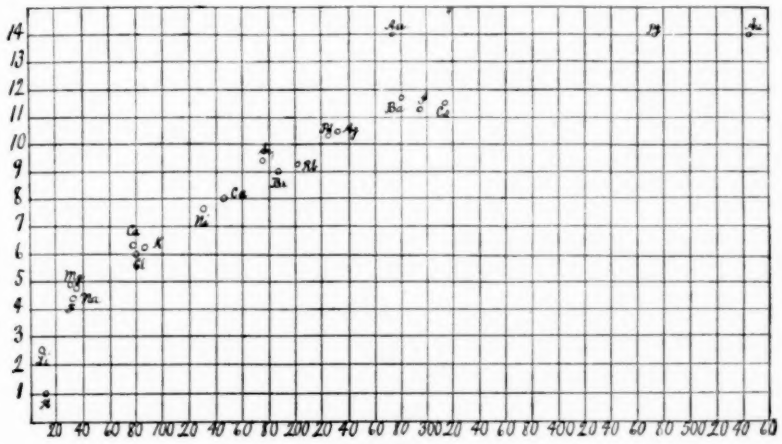

Fig. 1.

Other arguments which seem to the writer to strengthen the hypothesis that the positive subatoms of the elements have characteristic charges which vary as the square roots of their atomic weights may be found in the deflection of the positive ions of a Bunsen flame by an electric field, in the conductivity of flames charged with various salts and especially in the phenomena of chemical valence. The subject is discussed at greater length in a paper soon to appear in the Leland Stanford Jr. University publications.

STANFORD UNIVERSITY,
December 3, 1910.

ATOMIC CHARGES AND COHESION.

BY FERNANDO SANFORD.

IN a paper on positive atomic charges which has been accepted but has not yet been published by the PHYSICAL REVIEW it is shown that the positive subatoms apparently carry characteristic charges which are proportional to the square roots of their atomic weight, or more precisely, which may be calculated for atoms having an atomic weight greater than 13 from the equation $e = (\sqrt{W} - a)k$, where w is the atomic weight, a is a constant having a value of approximately 3.6 and k is a constant depending upon the system of units used.

Since writing the above paper I have become acquainted with the results of two other investigations which have an important bearing upon the theory of characteristic atomic charges. The first is a paper by A. von Antropoff in Roy. Soc. Proc., A, 83, 474, April 14, 1910, on the solubility in water of the gases of the Argon group. v. Antropoff's numbers for the solubility of these gases at 20 degrees are as follows: He, .0138; Ne, .0147; Ar, .0379; Kr, .0729; Xe, .0119.

Since cohesion is undoubtedly an electric attraction, and since we may expect the solubility of gases in water at a given temperature to be proportional to cohesion, these numbers suggest a method of calculating the relative magnitude of the charges carried by these monatomic molecules. If these numbers are proportional to the atomic charges, we should be able to calculate them from the formula $S = (\sqrt{w} - 3.6)k$, where S is the solubility factor and w the atomic weight of the element. The following table contains v. Antropoff's observed values of S and the values calculated from the above formula, letting $k = .014$.

It seems from the above table that with the exception of helium, whose charge cannot be calculated from our formula, but which is shown in the preceding paper to be much larger than is indicated

by theory, the solubility can be calculated from the above formula as closely as it can be measured.

Element.	w	S Obs.	S Calc.	Per Cent. Error.
He	4	.0138		
Ne	20	.0147	.0122	17
Ar	40	.0379	.0378	—
Kr	82	.0729	.0763	4.6
Xe	128	.1109	.1078	2.8

Average error = 6.1 per cent.

Another investigation which is related to the subject under consideration is one on the viscosity of the gases of the argon group, by Rankine, in Phys. Zeitsch., 11, 746, September, 1910. The bearing of Rankine's work on the subject under consideration rests on the fact that Sutherland, in a paper on "The Viscosity of Gases and Molecular Force," Phil. Mag., 36, 507, 1893, gives a formula for calculating a cohesion factor from the viscosity of gases. Rankine calculated Sutherland's cohesion factor, C, from his data and found the following values: He, 70; Ne, 56; Ar, 142; Kr, 188; Xe, 252. He calls attention to the evident misfit of helium in the series, and shows that for the other gases Sutherland's factor, $C = T_c/1.12$, where T_c is the critical temperature (absolute) of the gas. Calculated in this way, C should be very small for helium.

Since the cohesion between gas molecules must be due to the attraction of the positive subatoms of one molecule for the electrons of another molecule, these attractions would seem to be approximately proportional to the atomic charges, though here, since the electric fields of the electrons in the molecules of different gases cannot be assumed to be equal, as they can in the case of molecules of a single kind, we cannot look for the close agreement with the law which we find in the case of cohesion between gas molecules and water molecules. That is, in the case of solubility, each molecule is attracted by a group of water molecules which may be assumed to be equally charged in all cases, while here the attraction is between the electrical fields of similar molecules which are probably different for each gas.

The observed and calculated values of C are given below where, as before, $a = 3.6$ and where $k = 37$.

Element.	C Obs.	C Calc.	Per Cent. Error.
He	70		
Ne	56	32	43
Ar	142	100	30
Kr	188	202	7
Xe	252	285	13

Average error = 23 per cent.

The above values can be shown to vary much closer with the square root of the atomic weight than is indicated by the above table. Thus if $a = 2$ and $k = 27$, the following values are calculated:

Element.	C Obs.	C Calc.	Per Cent. Error.
He	70	0	
Ne	56	66	20
Ar	142	113	20
Kr	188	190	2
Xe	252	251	0

Average error = 5 per cent.

The above data seem to indicate that both the viscosity of gases and their solubility in water depend upon the characteristic charges carried by their molecules. Since most gaseous molecules are compound, consisting of two or more positive subatoms held together by their mutual attractions for one or more electrons, their charges are the resultant of the positive and negative charges of which they are composed and consequently cannot be calculated by the formula given above; but here the relation between their resultant charges and their critical temperature and solubility would probably hold. Hence, so long as the gas molecules or the water molecules are not dissociated by their mutual cohesion we would expect the solubility of gases in water to be related to their critical temperatures.[1]

[1] At the time when this paper was written I had not read a paper by R. D. Kleeman, entitled On the Nature of the Forces of Attraction between Atoms and Molecules which was published in the Phil. Mag. for May, 1910. In this paper Kleeman has calculated for a number of atoms a constant C_a, which determines the surface tension of the molecules in a liquid form to which the atoms belong, and has found this constant to vary as the square root of the atomic weight. Also, since this paper was in the hands of the Editors of the Physical Review Rankine has,

himself, published an article in the Phil. Mag. of Jan., 1911, in which he relates the viscosity of the inert gases to their atomic weight and gives the equation $N^2/A = 3.93 \times 10^{-10}$ in which N represents the viscosity factor and A the atomic weight. In this paper Rankine also gives the critical temperature of these gases as far as known and calculates it for neon and emanation. The values as given make the critical temperature almost exactly proportional to the square root of the atomic weights.

Since the melting points of the elements, as well as their critical temperatures depend upon cohesion, the melting points of the elements of a given group should vary as the square root of their atomic weights. Thus the melting points of the alkali metals can be calculated to within less than one per cent. from the equation $T = \frac{531.5}{\sqrt{w}} + 252.5$ in which T is the melting point (absolute) and w the atomic weight.

The compressibilities of several groups of elements can be calculated from similar formulæ as closely as they can be measured. The atomic refraction constants for a number of the elements, both as calculated by Edwards in Vols. 16 and 17 of the American Chemical Journal and by Eisenlohr in Zeit. phys. Chem., LXXV., 585, varies as the square root of the atomic weights. There can be no longer any doubt that this is the prominent factor in determining cohesion, nor that cohesion is an electrical force, hence it seems that the electrical charges of the atoms should also vary in some way with the square root of their atomic weights.

March 27, 1911.

STANFORD UNIVERSITY,
December 31, 1910.

A FORM OF NEUTRAL TINT ABSORBING SCREEN FOR PHOTOMETRIC USE.

BY HERBERT E. IVES AND M. LUCKIESH.

PERFECTLY neutral tint absorbing screens, suitable for reducing intensities with the photometer, or spectrophotometer, are not easily obtained. Certain neutral tint glasses on the market appear on measurement to be a mixture of "smoke" and cobalt blue. The "smoke" alone produces a yellow tinge, addition of cobalt blue produces a neutral tint, which is neutral only when the total transmission is viewed by the eye. It is a subjective gray, which on measurement reveals the characteristic absorption bands of cobalt blue, and such glasses are, as a consequence, useless for the spectrophotometer. Photographic screens have been spoken of as entirely non-selective. Those that we have prepared did not prove so on critical measurement, their defect being a progressive deficiency of transmission toward the shorter wave-lengths. Furthermore the large amount of scattering of light with them made their effective transmission vary with position to an unsatisfactory degree. Wherever possible there is one simple escape from these difficulties and that is the use of a rotating sectored disc. At other times the distance of the light source from the photometric screen may be changed. Occasions sometimes arise when neither the disc nor varying distance can be used, and in such cases the screens described below may be found useful.

In an investigation on the flicker photometer with spectral colors need was found for some means of reducing intensity in an entirely non-selective way, by known amounts. The dimensions of the source of light, and the distance at which it is used prohibit the use of the law of inverse squares. The sectored disc is barred because of the stroboscopic effects caused by it in conjunction with the periodicity of the flickering device of the photometer. Resort was had to a special form of neutral tint screen, namely an opaque-line grating on glass, of the type used by photo-engravers.

These screens are made by ruling fine lines through a wax layer, etching the glass and finally filling the grooves with opaque material, such as plumbago paste. They may be obtained as fine as 1,200 lines and as coarse as 40 or less lines to the inch. The relative sizes of the opaque and clear spaces may be varied in the ruling from equality to one and four (approximately) either way, or, if the ruling is coarse, the ratio may be larger. The transmission of such screens may therefore be anything from about 80 down to 20 per cent., and by using two together crossed, as low as three or four per cent. Examination with the spectrophotometer of screens of dimensions properly chosen, as described below, fails to detect any selective absorption.

The question of calibrating these gratings as absorbing screens brings up some points not to be overlooked in their use. The most important point is that the transmission depends not only upon the relative size of opaque and transparent spaces but upon the position, fineness, and dimensions of the grating. These variations in the transmission only become of considerable amount under certain conditions which may be termed extreme. It is shown below that proper choice of spacing may make the consequent errors negligibly small in most practical cases.

The light received upon the photometric screen consists of the central image, and a certain number of lateral spectra. The state of affairs is easily seen by holding the grating between the eye and a light source. The number of spectra visible depends upon the size of the grating and its position with respect to the eye and the light, and of course, on the fineness of the spacing. The amount of light falling at any point on the photometer screen is obtained by a knowledge of the number of spectra received from the grating and the quantity of light in each.

If θ is the angle of incidence, and ϕ the angle of emergence, the number of the order is given by

$$m = \frac{d}{\lambda}(\sin\theta + \sin\phi),$$

where d = grating spacing, λ = wave-length used.

Let D = distance between light source and photometer screen.

αD = distance between grating and screen.

βD = half width of grating.

Then

$$m = \beta \frac{d}{\lambda}\left(\frac{1}{\sqrt{\beta^2 + \alpha^2}} + \frac{1}{\sqrt{1 + \alpha^2 + \beta^2 - 2\alpha}}\right).$$

In Fig. 1 are plotted values of $m\lambda/d$ for various values of α and

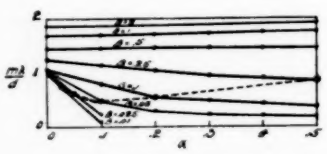

Fig. 1.

β. In Table I. are given the values of d/λ for various values of d at different wave-lengths. The product $m\lambda/d \cdot d/\lambda$ is at once the order, m, for the particular d studied. It is seen that when the grating is small with respect to the distance between source and screen (β small), the number of orders illuminating the latter varies markedly with the distance.

To determine what differences in illumination these differences in the number of orders cause, a formula given by Rayleigh[1] for the light in each order has been used. Let a and d be the widths of the transparent and opaque spaces respectively, m the order, B_0 the brightness of the central image, B_m the brightness of the mth spectrum, then

$$B_m : B_0 = \left(\frac{a + d}{am\pi}\right)^2 \sin^2 \frac{am\pi}{a + d},$$

also, if B is the brightness of the central image when the whole of the space occupied by the grating is transparent,

$$B_0 : B = a^2 : (a + d)^2.$$

These equations properly apply only to plane waves, *i. e.*, to the Fraunhofer class, while in using the gratings in the manner here considered we are dealing with the Fresnel class of diffraction phenomena. The errors will however be small. The light received on any linear element of a surface behind the grating, from a

[1] Lord Rayleigh, Scientific Papers, Vol. I., p. 213.

narrow line of light in front will be

$$I = B_0\left[1 + \sum_1^m \left(\frac{a+d}{am\pi}\right)^2 \sin^2 \frac{am\pi}{a+d}\right],$$

where the summation includes the orders on each side. The total light transmitted for $m = \infty$ will be $\frac{a}{a+d}B$, a quantity which the above expression approaches as a limit; the light transmitted up to any order m may then be expressed in percentage of $\frac{a}{a+d}B$. In Fig. 2 are plotted as curves the number of orders included,

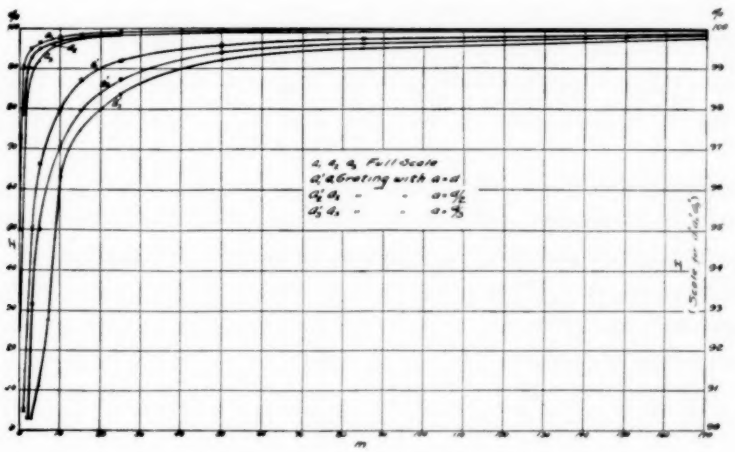

Fig. 2.

against the quantity I in per cent. of $\frac{a}{a+d}B$, for gratings in which $a = d$, $a = d/2$, $a = d/3$. The curves in Fig. 2 are plotted to two scales; a_1', a_2', a_3' on the larger scale are respectively a_1, a_2, a_3 magnified ten times.

For the present purpose it is not so important to study the absolute value of the total transmission,—this must be determined by experimental calibration. It is more important to study how the transmission varies with the variations in size and position which might occur in the practical use of the grating. Inspection of the curves shows that the transmission becomes constant to well within one per cent. after the fiftieth order, for the ratios of a

to d considered. It is only necessary that the extremes of the number of orders acting should both be high to secure any degree of constancy of transmission desired. By combining these data with those of Fig. 1 and Table I. we have everything necessary to solve any practicable case. Several such cases are next considered.

TABLE I.

Lines per Inch.	Lines per mm.	d (mm.)	d/λ (λ=.45μ)	d/λ (λ=.55μ)	d/λ (λ=.65μ)	d/λ (λ=.58μ)
50	1.97	.507	1126	921	780	874
100	3.94	.254	565	462	391	438
150	5.91	.169	376	307	260	292
200	7.88	.127	282	231	196	219
240	9.45	.1075	239	195	166	185
250	9.85	.1015	226	184	156	175
500	19.7	.0507	113	92.1	78	87.4

A grating of 7 cm. diameter, 240 lines to the inch, $a = d/2$ was available for experiment, and the following test was made to check the agreement between the calculated and experimental values of the transmission. The grating was placed between an incandescent lamp and the screen of a Lummer-Brodhun contrast photometer. The illumination on the screen was then measured for various

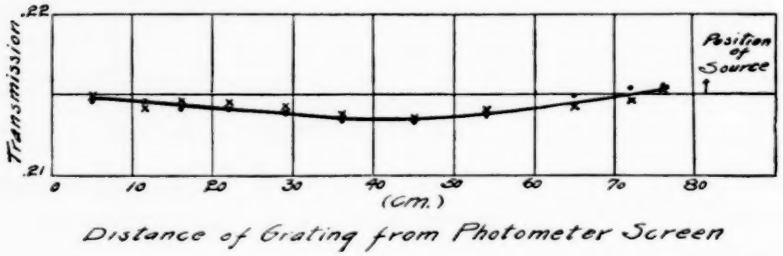

Fig. 3.

positions of the grating along the photometer track. A measurement of the illumination without the grating made possible a determination of the absolute values of the transmission. These are given in Fig. 3 and show a variation from 21.35 per cent. to 21.55 per cent., or a total variation of about 0.7 per cent. between the central position and the points 5 cm. from the lamp and screen.

The minimum at the center is in agreement with the curves of Fig. 1.

In order to find this variation by calculation we have $\beta = 3.5/81.5 = .043$. α varies from .5 at the center to $5/81.5 = .061$, at the points nearest to lamp and screen. Fig. 1 gives for the orders acting, $.17\ d/\lambda$ for $\alpha = .5$, and $.57\ d/\lambda$ for $\alpha = .061$. For λ we may take $.58\mu$, which closely represents the wave-length of maximum brightness in the present case; the orders are then (240 lines to inch) 31.5 and 105. from Table I. From Fig. 2 we obtain for $a = d/2$ values of I of 99.0 and 99.7. The difference between which agrees with the experimentally determined value.

This test indicates the reliability of the method of calculation, and so justifies applying it to the case of coarser or larger gratings, *i. e.*, to ones in which the variation in transmission is less than the one above measured. The case just considered is an extreme one, because in the first place the grating spacing is at least 5 times finer than is necessary for complete absence of line shadows on the photometer screen; in the second place, because one would not place a grating of this size so far from either light or screen under any practical conditions, as is the central position. Use of a grating of 50 lines to the inch would divide the error found by more than 5, *i. e.*, make it as small as .1 per cent. As the errors of the most careful photometric measurement is of the order of .5 per cent., an error of this size is small enough to be disregarded.

A case of some practical interest may be treated before drawing conclusions. Suppose a grating were used attached to a Lummer-Brodhun photometer head, that is, at a distance of about 5 cm. from the screen. Suppose it measured for absorption with the lamp at 100 cm.; what error would be introduced by using this value with the lamp at other distances? In this case α and β both vary. We must therefore take our values of $m\lambda/d$ from successive curves in Fig. 1. Thus, if the grating is 5 cm. wide we have at $D = 100$, $\alpha = .05$, $\beta = .025$; at 10 cm., $\alpha = .5$, $\beta = .25$, etc. These points are shown by the dotted line in the figure. These show a maximum value at $\alpha = .5$ (50 cm.) of .9, a minimum at $\alpha = .1$ (10 cm.) of .5. Applying these figures to the grating of 240 lines to the inch we have:

$$a = d/2, \quad \lambda = .58\mu,$$

$$m_{\max.} = .9 \times 185 = 166.5, \quad m_{\min.} = .5 \times 185 = 92.5.$$

$$I_{\max.} = 99.8 \text{ per cent.}, \quad I_{\min.} = 99.65 \text{ per cent.},$$

$$\text{difference} = .15 \text{ per cent.}$$

To within this degree of accuracy, therefore, the position of the light source is unimportant. A calibration made for one position holds for any position. With a coarser grating the calculated error is less, as discussed above.

This calculation includes two of the most usual cases of the use of absorbing screens; first, use on a photometer bar with the grating near the photometer screen and the light source at some distance; and second, the condition obtaining often with the spectrophotometer, namely, the light source quite near the diffusing surface. It appears then that a neutral tint screen of this character may be chosen which can be calibrated on an ordinary photometer bar, using sector discs or the law of inverse squares, and afterward used with negligible error with a spectrophotometer.

In the case of use with spectrophotometer it becomes of interest to investigate the possible selective transmission due to the different number of orders of different wave-lengths. If we take the minimum m from the last calculation, namely, $.5d/\lambda$ for the extreme wave-lengths $.65\mu$ and $.45\mu$ we obtain 83 and 119. From Fig. 2 we obtain for I_{83} and I_{119} respectively 99.6 per cent. and 99.7 per cent. or a selectiveness of 0.1 per cent. Here again the perfectly practicable coarser grating of say 100 lines to the inch would make this error still more negligible.

In the case of light sources and photometer screens of finite size the grating dimensions as calculated here need to be increased to secure very perfect uniformity of illumination. These calculations are however perfectly straightforward with the data given. Usually calculations as made above, on the basis of point source and point photometer screen, will be sufficient, especially if one allows a considerable "factor of safety" as has been done above by calculating the errors for a 240-line grating where a 100-line grating is quite fine enough.

Obviously gratings can be used for neutral tint screens only where the light is received on a diffusing reflecting surface, or diffusing glass. Where a bright filament is viewed or projected, gratings would be useless. However, a large part of practical photometric work conforms to the first condition. For certain special cases, where other means are not applicable these gratings should prove of use. Should the flicker photometer come into wide use, black line gratings would fulfil with it some of the functions of the sector disc with other forms of photometers.

A MICROSCOPE PLATE MICROMETER.

BY JOHN ZELENY AND L. W. MCKEEHAN.

IN the plate micrometer due to J. H. Poynting, for use with microscopes or telescopes, a plane parallel glass plate is tilted between the object and the eye-piece, shifting the image on the eye-piece cross-hairs in a direction perpendicular to the axis of rotation of the plate. By a suitable calibration, the angle of tilt necessary to place the images of two points in succession on a cross-hair parallel to this axis gives the distance between the points in the object. Poynting's adaptation of this micrometer to the microscope is described by A. H. R. Buller.[1] A plane parallel plate was inserted through a hole cut in the microscope tube. A rigid pointer gave the angular position of the plate on an attached scale.

The modified form of instrument to be described possesses certain advantages, and is especially adapted to the measurement of small objects or distances when a large number of such measurements is required.

The plate A of plane parallel glass is set just above the objective B, in the short tube C. To the ring D in which the plate A fits are attached the trunnions E, E, turning easily in bearings F, F, which are screwed into the sides of the tube C until they just touch D. At one end of the rotating system is the lever G, and at the other, the galvanometer mirror H. Both of these are carried on short sleeves adjustable about the axis. A counter-weight J serves to balance the moving parts so that the system remains in any position. The mirror H reflects light from a circular scale into the telescope K fastened to the barrel of the microscope by the rigid clamp L. The eye-piece of this telescope is conveniently near to that of the microscope. The circular scale is attached to the wall and the microscope stand is fixed with reference to it by guides or blocks, so as to be easily replaced in position. This scale should

[1] Researches on Fungi, 1909, p. 158.

be so far from the mirror that tenths of scale divisions need not be estimated.

A calibration curve or table giving the nearly linear relation between scale reading and displacement of object can be made for one magnifying power by direct measurement of a standard, and used for any other power by changing the scale of lengths.

The advantages of the plate micrometer thus improved can be summarized as follows:

The device can be attached to any microscope tube threaded for standard objectives, without marring the instrument.

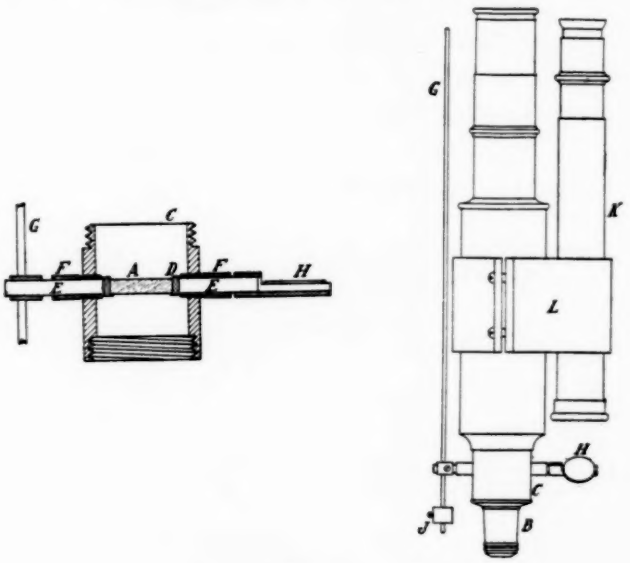

Fig. 1.

Any objective can be used with any eye-piece, giving a wide range of magnifications.

Different thicknesses of plate can readily be interchanged.

Back-lash, so troublesome in screw micrometers, is entirely absent.

The moving system is so light that its motion does not set up vibrations.

The use of a telescope avoids parallax and greatly increases the accuracy of scale reading. This would also be advantageous in the

ordinary form of plate micrometer where the plate is between object and objective.

Readings can be taken as rapidly as the accuracy of contact can be judged, since the plate can be tilted through its whole range in a fraction of a second, and the scale can be viewed by a slight motion of the head to one side.

The adjustment of telescope, mirror, and scale, is not affected by focusing the microscope.

Time is saved because it is not necessary to estimate tenths of scale divisions.

The instrument used in this laboratory has a glass plate 6 mm. thick, a circular scale of 131 cm. radius and 150 cm. long. Using Zeiss C objective and no. 5 eye-piece, giving a magnifying power of 325 diameters, the probable error in a single setting of the cross-hair on the edge of a small object was found to be 3 mm. on the circular scale, corresponding to .000003 cm. in the object. The maximum length measurable at this magnifying power is .0015 cm.

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